N. Y. State Library
JUN 2 6 1924

ABSTRACTS

OF

CHEMICAL PAPERS

ISSUED BY THE

BUREAU OF CHEMICAL ABSTRACTS

APRIL, 1924

BUREAU:

Chairman:
J. C. PHILIP, O.B.E., D.Sc., F.R.S.

Nominated by the Chemical Society:
J. I. O. MASSON, M.B.E., D.Sc.
G. T. MORGAN, O.B.E., D.Sc., F.R.S.
J. F. THORPE, C.B.E., D.Sc., F.R.S.
W. P. WYNNE, D.Sc., F.R.S.

Nominated by the Society of Chemical Industry:
E. F. ARMSTRONG, D.Sc., F.R.S.
J. L. BAKER.
E. V. EVANS, O.B.E.
Sir W. J. POPE, K.B.E., F.R.S.

A. PURE CHEMISTRY

Editor:
T. F. BURTON, B.Sc.

Assistant Editors:
H. M. DAWSON, D.Sc., B.Sc., Ph.D.
A. A. ELDRIDGE, B.Sc.
W. E. GARNER, M.Sc.
H. J. PAGE, M.B.E., B.Sc., A.I.C.
E. H. RODD, D.Sc.
E. E. TURNER, M.A., D.Sc.
H. WREN, M.A., D.Sc., Ph.D.

Adviser on Nomenclature:
A. J. GREENAWAY.

Indexer:
MARGARET LE PLA, B.Sc.

OFFICES OF THE BUREAU:
CENTRAL HOUSE, 46, FINSBURY SQUARE, LONDON, E.C. 2

Organic Chemistry.

Physical Properties of the Paraffin Hydrocarbons. R. E. Wilson and W. H. Bahlke (*Ind. Eng. Chem.*, 1924, **16**, 115—122).—Curves are presented between the following physical properties: vapour pressure and temperature, heat of vaporisation and vapour pressure, liquid density and temperature, and specific heat and temperature for the paraffin hydrocarbons from butane to tetracosane. These are compiled from published data and corrected and extended as follows: the vapour-pressure curve by Hildebrand's generalisation that the slope of the curve for any liquid is a constant if the vapour concentration is constant, with application of a correction based on Young's data for the lower members of the series; the heat of vaporisation on Hildebrand's similar rule that the molal entropy of vaporisation for all normal liquids is the same at equal vapour concentrations; the liquid density curve by the theorem of corresponding states. The critical data are calculated from Young's results and from the vapour-pressure curve. Only scanty specific heat data are available. [Cf. *B.*, 1924, 243.] C. I.

Characteristics of the Hydrocarbons in [American] Mid-continent Kerosene. C. R. Wagner (*Ind. Eng. Chem.*, 1924, **16**, 135—136).—The distillate from Oklahoma crude petroleum contains paraffins only in the most volatile fractions. When treated with half its volume of liquid sulphur dioxide at $-10°$, a fraction soluble in the latter is separated of similar boiling point but higher specific gravity, the proportion of this fraction to the whole rising with the boiling point. In the case of a kerosene, b. p. 198—244°, the SO_2-soluble fraction amounted to 5·4%. This fraction was subjected to repeated fractional distillation under reduced pressure, yielding four main fractions, the freezing points, indices of refraction, elementary analyses, and molecular weights of which were determined. The suggested formulæ are $C_{12}H_{18}$, $C_{14}H_{20}$, $C_{13}H_{18}$, and $C_{14}H_{18}$; it appears probable that these compounds are partly hydrogenated substituted naphthalenes. Their characteristic property, which is common to all SO_2-soluble fractions of this petroleum, is that they are readily nitrated even by dilute nitric acid. The SO_2-insoluble oil was similarly fractionated and examined. This fraction is unaffected by sulphuric acid ($d = 1·68$) and consists essentially of members of the *cyclo*hexane series. C. I.

Velocity of Oxidation of Paraffin Wax. I—IV. F. Francis [with W. F. Millard, C. H. Rutt, C. M. Watkins, R. W. Wallington, and C. P. Garner] (*J. Chem. Soc.*, 1924, **125**, 381—393).—Paraffin wax, obtained from shale oil and fusing at 55—56°, is oxidised exothermally by a stream of air or oxygen at 100—135°. Commencement of reaction is preceded by a latent period, after which the oxygen content rises to 11—16% in 70—1800 hours. The

latent period may be reduced by heating the wax, previous to oxidation, in a sealed vacuum (a treatment which does not alter the physical constants of the material, but slightly increases its solubility in chloroform and acetone), by the use of catalysts, and by previous treatment with sulphuric acid at 100°, which causes a loss in weight of about 5% of the material. Wax which, after being heated in a vacuum, was recrystallised from acetone had the same latent period as the untreated material. The latent period may therefore be ascribed to (*a*) the formation of a positive catalyst, (*b*) the destruction of a negative catalyst present in the original wax, or (*c*) isomeric change brought about by the action of heat, particularly the formation of unsaturated substances (cf. T., 1922, **121**, 498, 1534). Commencement of the oxidation is marked by the formation of carbon dioxide, and formic acid is always produced in the later stages of the reaction. The oxidation in presence of catalysts appears to take place in stages.

Wax treated at 100° with a stream of oxygen required 1060 hours to attain an oxygen content of 7%; with air at 100° the latent period was too long to determine, but at 120° an oxygen content of 7% was reached after 285 hours. Untreated wax in the presence of 5% of turpentine reached an oxygen content of 7% in 800 hours with air and in 320 hours with oxygen at 100°, in 285 hours with air at 120°, and in 46 hours with oxygen at 135°.

The temperature coefficient of the oxidation with oxygen is 1·6, whilst that of the latent period is 2·9. These values suggest that the rate of oxidation is governed by a physical process, but that the latent period is accompanied by a chemical change. Wax from lignite, having m. p. 46—47°, and containing 0·7% of oxygen, commenced to oxidise with oxygen at 135° after 10 hours, and contained 7% of oxygen after 24 hours. F. G. W.

Action of Iodine on Hydrocarbons. F. J. Nellensteyn (*Chem. Weekblad*, 1924, **21**, 102—106).—Iodine acts on all hydrocarbons, sometimes in the cold, but generally at high temperatures, forming hydrogen iodide, with separation of carbon and formation of colloidal carbon solutions. Treatment of paraffin oil at 160° gave a coal-like product, some 70% of the iodine added being driven off, mostly as hydrogen iodide, partly as free iodine. Reaction occurred at the ordinary temperature with a distillate from a Borneo asphaltic oil, *d* 0·886, b. p. 192—300°; at 160°, the iodine was converted nearly quantitatively into hydrogen iodide, carbon being formed both as a precipitate and in the colloidal condition. The results are interpreted as indicating reaction of the iodine with dissociation products of the hydrocarbons, containing only one carbon atom, *e.g.* $CH_3^{\bullet}$, $CH_2^{\cdot\cdot}$, and $CH^{\vdots}$. A highly unsaturated "cracked" gas-oil distillate, *d* 0·866, b. p. 58—150°, reacted with iodine very strongly at the ordinary temperature; the carbon which separated contained 30—37% of adsorbed iodine, not removable by thiosulphate or sodium hydroxide, but partly removed by alcohol. A high adsorbing power is to be expected, since the carbon is formed at low temperatures. The action of iodine is therefore analogous to that

of oxygen, in that hydrogen is removed from dissociation products containing only one atom of carbon, with separation of the latter in the colloidal condition, thus forming asphalt. S. I. L.

Acceleration of the Reaction between Ethylene and Sulphuric Acid. W. GLUUD and G. SCHNEIDER (*Ber.*, 1924, **57**, [*B*], 254—255).—The absorption of ethylene by sulphuric acid is catalytically accelerated by the presence of lead sulphate, calcium sulphate, ferric sulphate, anhydrous copper sulphate, or, particularly, ferric ammonium alum. The most suitable catalyst, however, is silver sulphate added to the extent of 0·5—1% of the weight of sulphuric acid; in contrast to the other catalysts, this material retains its activity over long periods, so that higher concentrations of ethyl hydrogen sulphate can be attained. It is readily recovered by electrolysis. H. W.

Contact Condensation of Acetylene. N. ZELINSKY (*Ber.*, 1924, **57**, [*B*], 264—276).—The pyrogenic condensation of acetylene in the presence of activated birch or lime charcoal has been studied; the adsorbent properties of the material give, in effect, the action of very greatly increased pressure without involving the dangers incurred in working with compressed acetylene. The method has the advantage that the temperature can be raised without danger to 600—650°, at which the process proceeds most advantageously, and that, in consequence of the presence of charcoal, the condensation occurs quietly and without explosion of the acetylene, which need not therefore be diluted with an indifferent gas. The deposition of carbonised matter on the contact material takes place to only a very minor extent, and the formation of solid hydrocarbons (cuprene) is not observed. Further hydrogenation of the aromatic hydrocarbons which are produced is scarcely observable. The main product of the change is benzene.

The most favourable conditions for the condensation of acetylene are secured when the gas is passed at the rate of 20 litres per hour through a hard glass tube, about 1 metre long and 1·5—2·4 cm. internal diameter, heated at 650°. The escaping gases consist mainly of acetylene containing some ethylene; the yield of tar exceeds 70% of that theoretically possible.

The tar is reddish-brown in colour and aromatic in odour. Colour and transparency depend considerably on the temperature and freshness of the contact agent. Its density varies according to the temperature of the experiment from 0·911 (600°) to 0·995 (660°), but never exceeds 1. It is separated by distillation into the following fractions: light oil, b. p. below 170°, 49·0% (45% below 150°); middle oil, b. p. 170—230°, 11·7%; heavy oil, b. p. 230—270°, 9·5%; anthracene oil, 21·2%; pitch, 6·8% (loss 1·8%). The preliminary fraction contains small amounts of diacetylene, CH:C·C:CH. The light oil consists mainly of benzene (35% of the tar) accompanied by small amounts of toluene and *p*-xylene (cf. A., 1923, i, 1169). The presence of styrene in the fraction, b. p. 140—150°, and of indene in the fraction, b. p. 150—180°,

is established. The middle oil solidifies at the atmospheric temperature to a yellow, crystalline mass, impregnated with liquid; it contains chiefly naphthalene. The green heavy oil contains large quantities of crystals of fluorene. The red anthracene oil deposits the hydrocarbon freely at the atmospheric temperature.

Reduction of the portion of the light oil boiling below 150° in the presence of nickel gives a mixture of cyclic hydrocarbons in which *cyclo*hexane predominates; it has b. p. 70—110°, d_4^{20} 0·7805, n^{24} 1·4238.

Acetylene is rapidly converted at 650° in the presence of active platinised asbestos into a pale yellow, transparent, aromatic tar, the yield being 45—50%; a portion of the acetylene, however, suffers decomposition in such a manner that the catalyst becomes coated with soot which ultimately inhibits the reaction; the tar is characterised by its very low content (5%) in pitch. Palladised asbestos is unsuitable for the condensation of acetylene. In the presence of pure, ignited asbestos, condensation of acetylene takes place at 650° with the production of a viscous, black, aromatic tar, d^{19} 1·000; the yield is about 40%. The action proceeds quietly without explosion, but cannot be continued over long periods on account of the deposition of soot. H. W.

Derivatives of Δ$^{\alpha}$-Butylene. M. DE MONTMOLLIN and P. MATILE (*Helv. Chim. Acta*, 1924, **7**, 106—111).—By the action of cold aqueous hypochlorous acid on Δ$^{\alpha}$-butylene, *butylene-α-chlorohydrin*, $CH_2Me{\cdot}CH(OH){\cdot}CH_2Cl$, is obtained as a colourless liquid, b. p. 141°. When oxidised with chromic acid, it gives chloromethyl ethyl ketone, a liquid with a pungent odour, b. p. 135—137°; this is also formed as a by-product with the butylenechlorohydrin, together with αβ-dichlorobutane and some higher chlorinated products, including (?)αβγ-*trichloro*-n-*butane*, b. p. 165—168°/725 mm. *Butylene α-bromohydrin*, prepared from α-butylene and hypobromous acid, is a colourless liquid, b. p. 56—58°/11 mm. By oxidation it gives bromomethyl ethyl ketone, b. p. 145°/725 mm. This ketone is also formed as a by-product with the bromohydrin, together with some αβ-dibromobutane and a *bromobutylene bromohydrin*, b. p. 79—80°. The above chloromethyl ethyl ketone gives with phenylhydrazine a *compound*, yellow crystals, m. p. 210—215° (decomp.), whilst bromomethyl ethyl ketone gives a *compound*, greenish-yellow crystals, m. p. 200—205° (decomp.). Both appear to contain two phenylhydrazine residues, and should be the same phenylhydrazido-phenylhydrazone; the difference cannot yet be explained.

α-*Butylene diacetate* is obtained by heating αβ-dibromobutane with fused potassium acetate and glacial acetic acid; it is a colourless liquid with an agreeable odour, b. p. 196—199°. When this liquid is saturated with gaseous hydrogen bromide, α-*bromo*-sec.-*butyl acetate*, $CH_2Me{\cdot}CH(OAc){\cdot}CH_2Br$, a pale yellow liquid, b. p. 76°/15 mm., is formed. α-*Butylene oxide*, $CH_2Me{\cdot}CH<\begin{matrix}CH_2\\|\\O\end{matrix}$, is formed by the action

of potassium hydroxide solution on the chloro- or bromo-hydrin; it is a colourless liquid, b. p. 58·5—59·0°. It is converted by 25% ammonia solution into *α-amino*-sec.-*butyl alcohol*, b. p. 168—170°.

E. H. R.

Alkaline Reduction of the Carbon Tetrahalides and of Potassium *aci*-Nitroform. R. O. Griffith and L. Hunter (*J. Chem. Soc.*, 1924, **125**, 463—464).—The carbon tetrahalides are effectively reduced by phenylhydrazine, arsenious oxide, or sulphites in alkaline solution. The action of acetone, hydrazine, antimonious oxide, and stannites is less certain. In the reduction of trichlorobromomethane to chloroform by means of aqueous sodium arsenite, dichlorobromomethane was not formed. Bromoform is reduced to methylene bromide by alkaline reagents, with the production of much formate, and chloroform is hydrolysed to formate without the production of methylene chloride. The action of alkaline reducing agents on potassium *aci*nitroform does not produce potassium dinitromethane, the salt being completely decomposed with the formation of ammonia. Hydrazine or phenylhydrazine reacts with evolution of nitrogen, a result which may explain the abnormally large production of nitrogen in the reaction between these compounds and tetranitromethane (T., 1923, **123**, 2305; and 1920, **117**, 880).

F. G. W.

Preparation and Reactions of the Dihalogenodinitromethanes. R. A. Gotts and L. Hunter (*J. Chem. Soc.*, 1924, **125**, 442—450).—The action of potassium hydroxide, iodide, cyanide, and nitrite, and of sodium thiosulphate, on the dihalogenodinitromethanes was investigated to test the hypothesis of Macbeth (T., 1922, **121**, 1118), that the activity of halogen atoms in similarly constituted molecules is the result of an induced positive polarity. In general, the stability of the compounds investigated conforms to the order Cl > Br > I, although in the case of the mixed dihalogenodinitromethanes exclusive removal of the more positive atom does not take place.

Potassium hydroxide reacts with dichloro- and dibromo-dinitromethanes according to the equation, $CCl_2(NO_2)_2 + 2KOH = CKCl(NO_2)_2 + KClO + H_2O$. In the case of chlorobromodinitromethane, the product is a mixture of the potassium salts of chloro- and bromo-dinitromethane. Chloroiododinitromethane behaves similarly to the chlorobromo-compound, losing more iodine than chlorine.

Potassium iodide reacts with the dihalogenodinitromethanes according to the equation, $CX_2(NO_2)_2 + 2KI = CKX(NO_2)_2 + KX + I_2$, both halogens being removed in part, but chlorobromodinitromethane gives also a small proportion of the iodo-salt.

Potassium cyanide behaves more energetically than the iodide, and both halogen atoms can be removed according to the equations, $CX_2(NO_2)_2 + KCN = CKX(NO_2)_2 + CNX$ and $2CKX(NO_2)_2 + 2KCN + H_2O = 2CKH(NO_2)_2 + KX + CNX + KCNO$; potassium chloro-

dinitromethane, however, remains unaffected on prolonged treatment with potassium cyanide.

Potassium nitrite acts as a reducing agent only in the case of chloroiododinitromethane, according to the equation, $CClI(NO_2)_2+2KNO_2=CKCl(NO_2)_2+KNO_3+NO+I$. The action of potassium nitrite in presence of carbonate on dibromodinitromethane is represented by the equations, $CBr_2(NO_2)_2+KNO_2+K_2CO_3=CK(NO_2)_3+KBr+KBrO+CO_2$, and $CBr_2(NO_2)_2+KNO_2+K_2CO_3=CKBr(NO_2)_2+KBr+KNO_3+CO_2$. Chlorobromodinitromethane yields the nitroform salt in much smaller proportion, and none is obtained from the dichloro-compound.

Sodium thiosulphate reduces potassium bromo- and iodo-dinitromethanes to potassium dinitromethane; the chloro salt is reduced much more slowly.

The action of acids on potassium bromodinitromethane is represented by the equation, $2CKBr(NO_2)_2+H_2SO_4=CBr_2(NO_2)_2+K_2SO_4+N+NO+CO_2+H_2O$. Potassium chlorodinitromethane behaves analogously. For the purposes of preparation, the direct action of halogens gives better yields than that of acids. Copper, lead, and ferrous salts have a similar action to that of mineral acids, but the silver monohalogenodinitromethanes can be obtained as stable, crystalline substances.

Dichloronitromethane is best prepared by the action of strong nitric acid on 2 : 4-dichloroacetanilide, and purified by conversion into the potassium salt, from which it is regenerated by the action of aqueous chlorine; it is a colourless oil, d_4^{25} 1·6616, not solidifying above −10°. Dibromodinitromethane, similarly purified, is a colourless, pungent oil, d_4^{25} 2·3946, m. p. 7·4°. *Potassium chlorodinitromethane*, light yellow prisms exploding at 83—85°, decomposes on keeping. *Silver chlorodinitromethane*, long, yellow needles, explodes at 80—81°. Chlorobromodinitromethane is best prepared in presence of sodium acetate, and forms a colourless, pungent liquid, d_4^{25} 2·0472. *Potassium iododinitromethane*, obtained by the action of iodine on potassium dinitromethane in aqueous solution, forms orange-yellow plates, exploding at 154°. It does not darken on exposure when pure. The *silver* salt forms insoluble, pale yellow, glistening leaflets, exploding at 109—110°. F. G. W.

Aliphatic Nitro-alcohols. II. R. Wilkendorf and M. Trénel (*Ber.*, 1924, **57**, [*B*], 306—309).—An extension of previous work (A., 1923, i, 288).

β-Chloro-β-nitroethyl alcohol condenses with acetaldehyde in aqueous solution, in the presence of a little potassium carbonate, to form *β-chloro-β-nitrobutane-αγ-diol*, $OH\cdot CH_2\cdot CCl(NO_2)\cdot CH(OH)\cdot CH_3$, long needles, m. p. 104°; with propaldehyde, it gives *β-chloro-β-nitropentane-αγ-diol*, colourless needles, m. p. 107° (decomp.). It does not appear to react with higher aldehydes.

The sodium derivative of β-chloro-β-nitroethyl alcohol is converted by methyl iodide in methyl-alcoholic solution into *β-chloro-β-nitropropyl alcohol*, m. p. 114°.

β-Chloro-β-nitroethyl alcohol is transformed by cautious treat-

ment with a mixture of nitric acid (*d* 1·4) and concentrated sulphuric acid into β-*chloro*-β-*nitroethyl nitrate*, a colourless liquid, d^{18} 1·568, which, when cautiously heated, decomposes into nitric acid and α-*chloro*-α-*nitroethylene*, a liquid, b. p. 54—55°/14 mm., which violently attacks the eyes; the latter substance can also be prepared by the action of phosphoric oxide on β-chloro-β-nitroethyl alcohol; in the presence of sodium hydrogen carbonate, it passes readily into a *polymeride*, m. p. 126—130° (decomp.), according to the manner of heating. H. W.

Preparation of Ethyl Ether by Williamson's Method. W. B. S. Bishop (*J. Soc. Chem. Ind.*, 1924, **43**, 23—24T).—Pure ethyl ether is obtained readily by Williamson's method, using ethyl iodide and sodium ethoxide. The yield is 80% of the theoretical (calculated on the ethyl iodide used). The oxidised copper gauze test for halogens is capable of detecting as little as 0·00004 g. of iodine present as ethyl iodide in 1 c.c. of ether. W. P. S.

Catalytic Dehydration of Ethyl Alcohol and Ether by Alumina. R. N. Pease and C. C. Yung (*J. Amer. Chem. Soc.*, 1924, **46**, 390—403).—The dehydrations were carried out in an electrically heated glass bulb of 35 c.c. capacity containing the alumina. The alcohol was run in from a burette at a uniform rate, and, when equilibrium conditions had been obtained, a test was made. It is found that appreciable quantities of ether as well as ethylene are formed from alcohol and that at 275° and 300° the amount of alcohol decomposed attains a maximum corresponding with about 65% conversion, whereas at 350° the reaction proceeds to complete dehydration with the production of ethylene. The maximum yield of ether was 60% at 250°. Ether decomposes readily at temperatures above 275°. The results are explicable on the theory that the dehydration of alcohol to ether is a reversible equilibrium corresponding with about 65% conversion, and that decomposition of the alcohol occurs in steps. Whilst the direct dehydration to yield ethylene is a possible mechanism, it is not necessary to assume it in order to account for the results. Water vapour and ethylene diminish somewhat the efficiency of the catalyst towards dehydration of alcohol. Alumina which has been used in the dehydration of ether appears to be peculiarly activated with respect to alcohol, and the yield of ethylene is nearly doubled. A. B. S.

Autoxidation of Ethers. A. M. Clover (*J. Amer. Chem. Soc.*, 1924, **46**, 419—430).—The oxidising properties acquired by ethyl ether when exposed to the air (A., 1922, i, 619) have been observed with several other ethers. In three cases, the ether peroxides have been obtained, whereas in the other cases, owing to the high boiling point of the ether, the peroxides could not be isolated. Aldehydes, esters, acids, and hydrogen peroxide were also formed. The hydrolysis of the peroxides, which yields acids, hydrogen peroxide, and aldehydes, is considered to occur in accordance

with the schemes: $OR{\cdot}CHR'{\cdot}O{\cdot}OH+H_2O \longrightarrow R'CHO+ROH+H_2O_2$ or $OR{\cdot}CHR'{\cdot}O{\cdot}OH \longrightarrow R'CO_2H+ROH$ or $R'CO_2R+H_2O$. The ethers experimented with were: propyl ether; *iso*propyl ether; *n*-butyl ether; *iso*amyl ether, b. p. 168—171°; methylenediethyl ether, b. p. 86—89°; benzylmethyl ether, benzylethyl ether, b. p. 183—185°; dibenzyl ether. In the case of propyl, *n*-butyl, and methylenediethyl ethers, the *peroxides* were isolated and analysed.

A. B. S.

Sulphochromic Oxidation and β-Oxidation. M. Polonovski (*Compt. rend.*, 1924, **178**, 576—578).—A study of the oxidation of aliphatic acids by means of dilute sulphuric acid–dichromate solutions at 100°. Acetic acid is unaffected. Propionic acid is oxidised slowly and incompletely, through pyruvic and acetic acids (α-oxidation). Butyric acid is oxidised rapidly, through acetoacetic acid (β-oxidation; α-oxidation is shown not to occur from a consideration of the oxidation–time curves). Valeric acid undergoes β-oxidation, which in this case produces propionic acid, oxidation decelerating as a result.

E. E. T.

Electrolysis of Potassium Oleate. G. W. F. Holroyd and J. E. W. Rhodes (*J. Chem. Soc.*, 1924, **125**, 438—442).—The apparent transport number of the oleic-ion in 0·2*N*-potassium oleate solution was found to be 0·725, in agreement with that obtained by McBain and Bowden (T., 1923, **123**, 2417) under different experimental conditions. Oleic acid is the chief product at the anode; neither oxygen nor oxidation products in amount demanded by the equation, $2R{\cdot}CO_2+H_2O=2R{\cdot}CO_2H+O$, were found. The apparatus used was a modification of Ostwald's, arranged to allow collection of gases evolved.

F. G. W.

Bromine Derivatives of α-Elæostearic Acid. M. Ishio (*J. Pharm. Soc. Japan*, 1923, No. 501, 789—796; cf. T., 1903, **83**, 1042; 1912, **101**, 2082; Nicolet, A., 1921, i, 390).—Dibromo-α-elæostearic acid (73 g.), colourless plates, m. p. 91°, is prepared by adding bromine to a solution of α-elæostearic acid (150 g.) in ether or light petroleum cooled below −15°; if chloroform is used as solvent, a tetrabromide (35 g.), m. p. 115°, is produced from the acid (100 g.) or from the dibromide. The dibromide is changed by alcoholic potassium hydroxide solution into a viscous oil free from the halogen, the reduction of which with hydrogen in the presence of platinum black yields stearic acid. When the tetrabromide is treated with alcoholic potassium hydroxide, a dibromide, $C_{18}H_{30}O_2Br_2$ or $C_{18}H_{32}O_2Br_2$, lustrous crystals, m. p. 40—40·5°, is produced.

K. K.

Perilla Oil. III. Bromides of the Linolenic Acids of Perilla Oil. K. H. Bauer (*Chem. Umschau*, 1924, **31**, 83—86; cf. A., 1923, i, 180).—Considerable quantities of linolenic acid hexabromides, prepared from perilla oil, were debrominated with zinc and alcohol and the linolenic acid obtained was brominated

again. The precipitated bromides were separated. The soluble bromides were then debrominated and the separated fatty acids submitted to oxidation by Hazura's method. The solid oxidation products were mixed with sand and extracted in succession with boiling ether, light petroleum, and alcohol. From the alcoholic extract a small quantity of an acid, m. p. 143—147°, was obtained. The aqueous solution of the soluble oxidation products yielded a small quantity of a yellowish-brown oil and linusic acid, m. p. 203°. *iso*Linusic acid was not found. The hexabromides obtained from perilla oil were satisfactorily recrystallised from boiling xylene, whereby hexabromostearic acid, m. p. 179—181°, was isolated. All attempts to separate the product into components by fractional crystallisation of large quantities were without effect, so that the substance is presumably homogeneous. Owing to the uncertainty surrounding the oxidation of and formation of additive compounds from these highly unsaturated substances, it is not considered safe to assume that, because linusic acid is the only hydroxy acid obtained from the soluble brominated linolenic acids, the oxidation of β-linolenic acid yields this acid only. Attempts to prepare hexahydroxystearic acids from hexabromostearic acids by treating them with silver oxide were unsuccessful. The effect of allowing perilla oil to remain for a long time in the dark in contact with a small quantity of iodine (conditions favourable to the transformation of α- into β-elæostearic acid in the case of tung oil) was studied; steric rearrangement did not occur under the conditions chosen.

H. C. R.

Glycerides of Lard. II. Synthetical. C. Amberger and A. Wiesehahn [and, in part, J. Bauch] (*Z. Unters. Nahr. Genussm.*, 1923, **46**, 291—299).—α-Oleo-βγ-distearin [glyceryl α-oleate βγ-distearate], m. p. 42°, was synthesised by Fischer and Pfähler's method (A., 1920, i, 807) from α-mono-olein and stearyl chloride. α-Palmito-αβ-diolein, synthesised in a similar manner from α-monopalmitin and oleyl chloride, is a dark yellow oil which solidifies at 0°. Attempts to synthesise oleopalmitostearin were unsuccessful. A comparison of the properties of the mixed glycerides isolated from lard with those synthesised (cf. A., 1922, i, 804) and those obtained by their hydrogenation, leads to the conclusion that the following are present: β-palmito-αγ-distearin, β-stearo-αγ-dipalmitin, α-oleo-αβ-distearin, α-palmito-αβ-diolein, and probably β-oleo-α-palmito-γ-stearin.

H. C. R.

Crystalline Bromides of Linseed Oil. H. Toms (*Analyst*, 1924, **49**, 77—81).—A substance, m. p. 153° (corr.), is obtained by successive treatment of the crude bromide from linseed oil with ethyl acetate, alcohol, and ether. Its analysis agrees closely with the formula, $C_{57}H_{94}O_6Br_{16}$, from which it is concluded that it is a linolic–dilinolenic bromoglyceride. Its solubility in ethyl acetate at 15—20° is 0·15—0·20 g. per 100 c.c. The residue obtained from the ethyl acetate mother-liquor yields a small amount of material, m. p. 117° (corr.). The analysis of this substance corresponds

approximately with the formula, $C_{57}H_{98}O_6Br_{12}$, and it may be trilinolic bromoglyceride or an oleic–linolic–linolenic bromoglyceride. Attempts were made to determine the bromide which was insoluble in ethyl acetate, and there were indications that the amount of the most unsaturated glyceride in linseed oil is a constant proportion of the total unsaturated substances present. H. C. R.

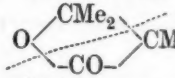
Uncommon Animal Fats. W. N. Rae (*Analyst*, 1924, **49**, 83—84).—The analytical characters of the fats of the following wild animals of Ceylon are given: leopard (*Felis pardus*), sambhur (*Cervus unicor*), spotted deer (*C. axis*), peafowl (*Pavo cristatus*), and wild boar (*Sus cristatus*). The values for leopard's fat agree closely with those given by Lewkowitsch for tiger's fat, and the values for the two members of the deer tribe agree with those of the chamois. European wild boar fat, however, differs considerably from that of the Ceylon wild boar. [Cf. *B.*, 1924, 264.] H. C. R.

β-Lactones of β-Hydroxybutyric Acid and its Alkyl Derivatives and the Influence of Constitution on the Decomposition of β-Lactones. H. Salkowski, jun. (*J. pr. Chem.*, 1923, **106**, 253—265).—When α-dialkylated β-hydroxybutyric acids are distilled they decompose into acetaldehyde and a dialkylacetic acid. A somewhat similar reaction to this is the thermal decomposition of methyl β-hydroxy-α-methyl*iso*propylmalonolactone, $O<\begin{matrix}CMe_2\\CO\end{matrix}>CMe\cdot CO_2Me$, into acetone, dimethylketen, and carbon dioxide. To determine whether the decomposition of the β-hydroxybutyric acid may be preceded by the intermediary formation of a β-lactone which then decomposes into aldehyde and keten, the latter subsequently taking up the elements of water, β-lactones of β-hydroxybutyric acid, β-hydroxy-α-ethyl- and β-hydroxy-αα-dimethyl-butyric acids, were prepared and their thermal decomposition was studied.

The required hydroxybutyric acid derivatives were prepared by reduction of the corresponding derivatives of ethyl acetoacetate with sodium amalgam. *β-Hydroxy-α-ethylbutyric acid* is a viscous liquid, b. p. 123°/0·8 mm. *β-Hydroxy-αα-dimethylbutyric acid* forms a viscous liquid, b. p. 108—110°/0·02 mm., which slowly crystallises to bunches of needles, m. p. 34°. Part of the acid is converted into an *anhydride*, $OH\cdot CHMe\cdot CMe_2\cdot CO\cdot O\cdot CHMe\cdot CMe_2\cdot CO_2H$, b. p. 200—203°/15 mm., a very viscous liquid. The β-hydroxy-acids were converted into β-bromo-acids. For this purpose β-hydroxybutyric acid and β-hydroxy-α-ethylbutyric acid had first to be converted by distillation into the corresponding crotonic acid and the product treated with liquid hydrogen bromide. *β-Bromo-α-ethylbutyric acid* is a yellow, viscous liquid, b. p. 140—143°/15—16 mm.; *β-bromo-αα-dimethylbutyric acid* forms brown needles, m. p. 42°, b. p. 115°/0·2 mm. The lactones were obtained by treating the acids with sodium carbonate solution and extracting with ether. α-Ethyl-β-butyrolactone has b. p. 75°/13 mm. (cf. Johansson and Hagman, A., 1922, i, 426) and *αα-dimethyl-β-butyrolactone* has b. p. 63—65°/14 mm. The thermal decomposition of the lactones in each

case gave carbon dioxide and an olefine, β-butyrolactone giving propylene, α-ethyl-β-butyrolactone giving amylene, and αα-dimethyl-β-butyrolactone giving α-methylbutylene. The decomposition is therefore different from that of the αα-dialkyl-β-hydroxybutyric acids.

The type of β-lactone decomposition occurring in the case of methyl β-hydroxy-α-methyl*iso*propylmalonolactone,



the so-called ketone-splitting, can probably only take place when the β-carbon atom is tertiary. E. H. R.

Condensation between Pyruvic Acid and Formaldehyde. Y. ASAHINA and S. TERADA (*J. Pharm. Soc. Japan*, 1923, No. 502, 855—878).—The action of pyruvic acid on formaldehyde gives a compound, $C_9H_8O_6$, colourless plates, m. p. 239—240° (decomp.), which is shown to be methylenebis-α-ketobutyrolactone,

$$\begin{matrix}CO\cdot CO\\ |\\ O-CH_2\end{matrix}>CH\cdot CH_2\cdot CH<\begin{matrix}CO\cdot CO\\ |\\ O-CH_2\end{matrix}.$$

It gives the following derivatives: *ammonium* salt, $C_9H_7O_6\cdot NH_4$, white, silky crystals; *potassium* and *sodium* salts; unstable *silver* salt, $C_9H_6O_6Ag_2$, white scales; *ethyl* ester, m. p. 124—125°; monoacetyl derivative, scales, m. p. 135°; *dibenzoyl* compound, m. p. 122°; *phenylhydrazine* salt, $C_9H_8O_6,(Ph\cdot NH\cdot NH_2)_2$, white crystals, m. p. 195—196°; *phenylhydrazone*, $C_9H_8O_4(N\cdot NH\cdot Ph)_2$, m. p. 225—227° (decomp.); *semicarbazide* compounds, m. p. 196—197° (decomp.), and m. p. 182—183° (decomp.), respectively; *chloro*-compounds, m. p. 151—152°, and m. p. 183—184°. When heated at 145° with concentrated sulphuric acid, it yields an anhydride, $C_9H_6O_5$, white crystals, which do not melt below 300°.

Methylenebis-α-ketobutyrolactone is oxidised by silver oxide to the *substance*, $CH_2<\begin{matrix}C(CH_2OH)\cdot CO\\ |\\ C(CO_2H)-CH_2\end{matrix}>O$, colourless, hexagonal crystals, m. p. 185—185·5°. It is not coloured by ferric chloride, but gives the pine-shaving reaction and contains one carboxy group, one lactone ring, and one hydroxy group. It yields a *methyl* ester, silky crystals, m. p. 105—105·5°, a *monoacetyl* derivative, m. p. 130°, and *monobenzoyl* compound, m. p. 130—131°. When heated with hydriodic acid and red phosphorus, it gives two iodine *compounds*, $C_7H_{10}O_4I_2$, m. p. 168—169° and 143—144°, respectively. When reduced with sodium amalgam, the former iodine compound gives *cis*-αγ-dimethylglutaric acid and the other the *trans*-isomeride. It is oxidised by fuming nitric acid to the *dicarboxylic acid*,

$$CH_2<\begin{matrix}C(CO_2H)-CO\\ |\\ C(CO_2H)\cdot CH_2\end{matrix}>O,$$

white crystals, m. p. 219—220°, which gives the pine-shaving reaction and contains two carboxyl groups and one lactone ring. Its *dimethyl* ester, prisms, melts at 77·5—78·5°. By heating with hydriodic acid and red phosphorus, it gives an iodine *compound*,

$C_6H_8O_4I_2$, m. p. 167—168°, the reduction of which with sodium amalgam produces αα-dimethylsuccinic acid. The similarity between the relation of β-tetronic acid to methylenebis-β-tetronic acid and that of α-tetronic acid to methylenebis-α-ketobutyrolactone was observed spectrographically. K. K.

Influence of Strong Acids on the Solubility of Oxalic Acid. W. HERZ and E. NEUKIRCH (*Z. anorg. Chem.*, 1923, **131**, 303—309).—The solubility of oxalic acid is depressed by the addition of a strong acid (hydrochloric, sulphuric, nitric) up to a certain concentration of the latter, after which it is increased. No action could be detected between oxalic and sulphuric acids up to a 3·5-molar concentration of the latter. Nitric acid exerts an oxidising effect, apparently due to impurities, and the figures obtained with this acid are not accurate. The results obtained are compared with those calculated on the solubility-product principle, the agreement being fair except in the case of nitric acid. [Cf. *B.*, 1924, 277.] S. K. T.

Photochemical Sensitisation of the Maleic Ester Transformation by means of Bromine. J. EGGERT [with W. BORINSKI] (*Physikal. Z.*, 1924, **25**, 19—21).—A study of the transformation of maleic ester in carbon tetrachloride solution, in presence of bromine, into fumaric ether, under the influence of energy of wave-lengths 557, 436, and 365 μμ, gave the following results:—(1) The photochemical efficiency at 18° with blue light (436 μμ) is 565, much greater than the figure calculated from the equivalent law. (2) The transformation is proportional to the number of absorbed quanta, but independent of the concentrations of bromine and solvent within wide limits; it is proportional to the quantum dimension at uniform temperatures, and increases for the same radiated energy exponentially with the temperature. These results appear contradictory, and seem to indicate that the activated molecule can survive several collisions. S. I. L.

Correlation of Additive Reactions with Tautomeric Change. II. Reversibility in Relation to the Stability of Carbon Chains. E. H. INGOLD (USHERWOOD) (*J. Chem. Soc.*, 1924, **125**, 435—438).—Failure to obtain a homologue by the method which leads to the formation of the parent substance may be due to the structure of the homologue admitting of some retrograde additive reaction by which it can break down. The influence of homology on the reversibility of such addition reactions thus becomes the determining factor in the ability to exist of various types of carbon structure.

The influence of homology on the reversibility of the aldol addition process is very marked. Thus in the cases of acetaldehyde, *iso*butaldehyde, and α-methylbutaldehyde, the percentages of aldol present in the equilibrium mixtures at 25° and 62° are, respectively, 100, 92 and 39, and 41 and 9. The failure of Neustädter (A., 1907, i, 14) to obtain α-methylbutaldehyde must be ascribed to the experimental limitations imposed on the aldol reaction by the

influence of temperature and structure on its reversibility. In the case of acetaldehyde, reversibility could not be detected at the ordinary temperature, and experiments at 60° were rendered impossible by the formation of crotonaldehyde.

The position of the equilibrium, in the case of α-methylbutaldehyde, was determined by keeping the aldehyde or aldol, mixed with an equal volume of saturated aqueous potassium carbonate, in a closed vessel at a known temperature for a definite time, and working up as previously described (T., 1923, **123**, 1723), except that the distillation was finished at 125° in an atmosphere of carbon dioxide. α-*Methylbutaldol* forms a rather viscous, colourless liquid, b. p. 103—104°/6 mm., with a characteristic earthy odour.

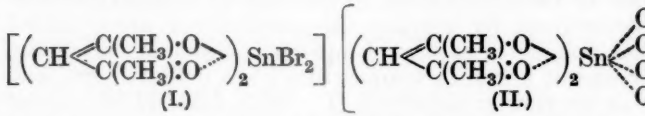
F. G. W.

Dichloroacetaldoxime. O. Routala and W. Nevvius (*Ber.*, 1924, **57**, [*B*], 252—254).—*Dichloroacetaldoxime*, $CHCl_2{\cdot}CH{:}N{\cdot}OH$, a colourless liquid with a penetrating odour, b. p. 67—69°/17 mm., 40—44°/2—3 mm. (partial decomp.), is prepared by the action of hydroxylamine hydrochloride on crude dichloroacetaldehyde obtained from trichlorolactic acid. It is converted by hydroxylamine at the atmospheric temperature into glyoxime. With phenylcarbimide, it yields the *compound*, $C_9H_8O_2N_2Cl_2,C_6H_6$, which darkens at 155° but has not a definite m. p. Attempts to transform it into the monoxime of glyoxal were not successful. H. W.

Condensation Products of Diethyl Ketone. J. B. Ekeley and M. S. Carpenter (*J. Amer. Chem. Soc.*, 1924, **46**, 446—450; cf. Ekeley and Howe, A., 1923, i, 997).—The protracted action of an excess of diethyl ketone on sodium ethoxide at 10° leads to the production of a mixture of *homomesityl oxide* [*γ-ethyl-δ-methyl-Δ$^{\gamma}$-heptene-ε-one*], $CEt_2{:}CMe{\cdot}COEt$, and *homoisophorone*, $C_{15}H_{28}O$. The former substance is a colourless liquid with a strong, mint-like odour and taste, b. p. 98—102°/20 mm., d_4^{20} 0·8535, n_D^{20} 1·4501. Homo*iso*phorone is a pale yellow, slightly viscous liquid, b. p. 137—140°/8 mm., d_4^{20} 0·91456, n_D^{20} 1·4831. A. B. S.

Residual Affinity and Co-ordination. XVII. Stannic Derivatives of β-Diketones. G. T. Morgan and H. D. K. Drew (*J. Chem. Soc.*, 1924, **125**, 372—381).—The product of the reaction between molecular proportions of stannic chloride and acetylacetone in chloroform solution is a white, crystalline precipitate, m. p. 150° (decomp.), which deliquesces rapidly in air with formation of a crystalline substance, m. p. 98°. If instead of isolating this product, the reaction mixture is boiled with a second molecular proportion of acetylacetone, stannic bisacetylacetone dichloride, m. p. 202—203°, is obtained. This substance, contrary to Dilthey's statement (A., 1906, i, 342), is soluble in hot benzene, and its molecular weight in that solvent corresponds with the monomeric formula, $Sn(C_5H_7O_2)_2Cl_2$. The corresponding dibromide, obtained by the interaction of stannic bromide and copper acetylacetone in chloroform solution, does not react with stannic bromide when the two substances are dissolved together in anhydrous solvents, but

the introduction of water leads to the formation of tetra-aquostannic bisacetylacetone stannibromide, $[(H_2O)_4Sn(C_5H_7O_2)_2]SnBr_6$. Stannic bisacetylacetone dibromide (I) and the tetra-aquo compound (II) exhibit co-ordination numbers of six and eight, respectively.



(I.) (II.)

The formation of stannic bis-β-diketone dibromides is a general reaction between stannic bromide and the copper salts of the β-diketones in chloroform, and proceeds according to the following equations: $3SnBr_4+3CuAc_2=3SnAc_2Br_2+3CuBr_2$; $3CuBr_2+CuAc_2=2Cu_2Br_2+2AcBr$, where Ac is the univalent β-ketonic chelate group and AcBr the corresponding bromo-β-diketone. The *cis-trans* (octahedral) isomerism theoretically possible has not yet been detected among these co-ordination compounds.

Stannic bisacetylacetone dibromide, transparent, colourless, lustrous, six-sided prisms, or aggregates of flaky crystals, m. p. 187°, separates from benzene as the double compound $[SnBr_2(C_5H_7O_2)_2]_2,C_6H_6$, which loses the solvent at 70—110°. *Tetra-aquostannic bisacetylacetone stannibromide*, obtained as described above or by the interaction of stannic bromide and stannic *bis*acetylacetone dibromide in presence of moisture, forms large, transparent, colourless prisms, m. p. 105—107°. When boiled with benzene, it loses water and dissociates into stannic bromide and the bisacetylacetone dibromide. *Stannic bisbenzoylacetone dibromide* is a white, microcrystalline powder, m. p. 213—214°, soluble in hot acetylacetone, with which it reacts to form benzoylacetone and the *bis*acetylacetone dibromide. *3-Bromobenzoylacetone* was isolated as colourless prisms with an aromatic lachrymatory odour, m. p. 43—45°. *Stannic bisdibenzoylmethane dibromide*, shining, sulphur-yellow crystals, m. p. 276—278°, is only slowly hydrolysed by aqueous potassium hydroxide (40%) with formation of acetophenone. *Stannic bis-3-ethylacetylacetone dibromide*, transparent, colourless, six-sided prisms, m. p. 164—166° after softening at 162°, and *3-bromo-3-ethylacetylacetone*, a pale yellow, lachrymatory liquid, b. p. about 195°, are described. F. G. W.

The α- and β-Forms of certain Monosaccharides. O. Svanberg and K. O. Josephson (*Ber.*, 1924, **57**, [*B*], 297—299).—It is proposed to discriminate between the α- and β-forms of monosaccharides by observation of their differing affinity towards invertase. In the cases of dextrose and xylose, a distinct difference is observed in the behaviour of the two forms of the sugar; the α-variety of one sugar resembles exactly the β-variety of the other.

Amongst the monosaccharides, certain instances are encountered in which the more strongly dextro-rotatory variety (the α-form according to Hudson) can only be converted slowly, if at all, into the corresponding acetone-sugar, whereas in others (pentoses) the

α-variety readily undergoes this change. When the α-sugar is very inert, the β-sugar is highly active.

The conclusions based on the two methods are identical in the cases of dextrose and xylose, but the available experimental data are insufficient to permit an extended proposal for the designation of α- and β-forms. H. W.

Molecular Configuration in the Sugars and Acid Production by *Bacillus Granulobacter Pectinovorum*. H. B. SPEAKMAN (*J. Biol. Chem.*, 1923, **58**, 395—413).—The non-volatile acid produced during the fermentation of starch by *Bacillus granulobacter pectinovorum* (cf. Reilly, Hickinbottom, Henley, and Thaysen, A., 1920, i, 465) has been identified as lactic acid, and the rates of formation of this acid, as well as those of acetic and butyric acids, during the fermentation of starch, arabinose, xylose, dextrose, galactose, and mannitol have been studied. From the results obtained, the fermentation of dextrose is provisionally regarded as taking place in two ways, according to the following schemes (cf. also A., 1920, i, 797):

(I.) Dextrose → acetic acid → H_2+CO_2.
Dextrose → acetic acid → acetaldehyde → ethyl alcohol.
Dextrose → butyric acid → butaldehyde → butyl alcohol.
Dextrose → butyric acid → acetoacetic acid → acetone+CO_2.

(II.) Dextrose → lactic acid → acetic acid (?) → H_2+CO_2.

The author also tentatively advances the theory that the rupture of the sugar molecule takes place preferentially and most rapidly between those carbon atoms the hydroxyl groups of which are adjacent to one another. On this basis, mannose, which contains two pairs of adjacent hydroxyl groups, would be expected to be fermented more rapidly than dextrose or galactose, which only contain one such pair. Further, whereas the fermentation of dextrose should proceed mainly according to scheme (I), that of galactose should proceed mainly according to scheme (II). These deductions appear to be confirmed by experiment. Similar deductions from the configurations of the pentoses are also in accord with fact, but the theory appears to fail with respect to dulcitol, which, unlike mannitol, is not fermented by the bacillus (cf. also Robinson, A., 1922, i, 971). E. S.

Relations between Rotatory Power and Structure in the Sugar Group. I. The Halogenoacyl and Nitroacyl Derivatives of the Aldose Sugars. C. S. HUDSON (*J. Amer. Chem. Soc.*, 1924, **46**, 462—477).—Investigations have been carried out with a view to determine the probable structure and physical constants of the as yet undiscovered α-halogenoacetylglucoses and related sugars as a help to their syntheses.

The application of van't Hoff's hypothesis of additive optical

superposition to the two forms of dextrose penta-acetate permits the calculation of the rotation of the acetylated basal chain which is common to both varieties. If this value is subtracted from the known rotation of acetylbromoglucose, the numerical value for the halogenated carbon atom can be deduced. An extension of this method of calculation to a series of halogenoacetyl- and nitroacetyl-glucoses shows that the rotation of the terminal asymmetric carbon atom in these compounds is approximately a constant quantity for the various aldoses. A comparison of the calculated and observed values for a series of halogenoacetyl sugars, such as bromo- and chloro-acetyldextrose, indicates that they are to be classified as α-forms instead of, as previously, β-varieties.

Van't Hoff's theory is applicable also to the glucosamines and to derivatives of deoxyglucose. Bromoglucodesose tribenzoate (Bergmann, Schotte, and Leschinsky, A., 1923, i, 653), is an α-derivative whereas deoxymethylglucoside tribenzoate prepared from it is a β-form. Toluene-*p*-sulphonyltriacetylbromoglucose (Freudenberg and Ivers, A., 1922, i, 524) is also an α-variety, whereas the corresponding tetra-acetate and the methylglucoside belong to the β-series. A. B. S.

Relations between Rotatory Power and Structure in the Sugar Group. II. The Halogenoacetyl Derivatives of a Ketose Sugar [*d*-Fructose]. C. S. Hudson (*J. Amer. Chem. Soc.*, 1924, **46**, 477—483; cf. preceding abstract).—The theory of optical superposition may be applied to ketoses, the effect of the halogenated terminal carbon atom being of the same magnitude as for the aldoses.

In the case of the two isomeric lævulose penta-acetates, the calculated values for $[\alpha]_D$ are $-5°$ and $-103°$ in chloroform, whereas the observed rotations of the two known isomerides are $[\alpha]_D^{20}$ $+34·7°$ and $-121°$ in the same solvent. It seems very unlikely that the dextrorotatory form is the expected α-derivative; possibly it has a different ring structure from the compounds hitherto examined. The other isomeride, $[\alpha]_D^{20}$ $-121°$, may be the β-form, although a difference of 18° causes doubt; the fact that normal β-bromo- and fluoro-acetyl-lævuloses can be prepared from it are evidence in favour of the β-modification. A. B. S.

Relations between Rotatory Power and Structure in the Sugar Group. III. The Biose of Amygdalin [Gentiobiose] and its Configuration. C. S. Hudson (*J. Amer. Chem. Soc.*, 1924, **46**, 483—489).—The identity of the biose of amygdalin with gentiobiose is established by the observation that the rotation of the biose chain of amygdalin, as calculated from the rotations of two of its derivatives, *iso*amygdalin and prulaurasin, has the same value as the rotation of the chain of gentiobiose. The line of evidence is entirely independent of that of Haworth and Leitch (T., 1922, **121**, 1921) or Kuhn (A., 1923, i, 589). The combined results prove the configuration of gentiobiose to be that of 1 : 6-β-glucosidoglucose. Maltose and gentiobiose are the α- and β-glucos-

idic forms respectively of 1 : 6-glucosidoglucose; they constitute the first αβ pair of compound sugars to be definitely allocated.
A. B. S.

Polysaccharides. XXII. Lichenase and Reserve Cellulose [Lichenin]. XXIII. The Separation of Lichenase into Constituent Enzymes. P. KARRER and others.—(See i, 471.)

Polysaccharides. XXIV. The Occurrence of Lichenin (Reserve Cellulose) in Lichens and other Plants. P. KARRER, M. STAUB, and J. STAUB (*Helv. Chim. Acta*, 1924, **7**, 159—162).—The preparation of lichenin is described from the lichens *Evernia vulpina*, *Usnea barbata*, L., and *Parmelia furfuracea*, Ach.; it is shown to be identical with that from Iceland moss, *Cetraria Islandica*. It also occurs in many other plants, such as barley, oats, maize, spinach, beans, hyacinth bulbs and others. [Cf. i, 471.]
E. H. R.

Starch Iodide. A. LOTTERMOSER (*Z. angew. Chem.*, 1924, **37**, 84—85; cf. this vol., i, 269).—The partition of iodine between starch, aqueous potassium iodide, and carbon tetrachloride was determined, using the partition coefficient of iodine between carbon tetrachloride and $N/10$-potassium iodide (=1·16 at 25°). The partition of iodine between carbon tetrachloride, aqueous potassium iodide, and soluble starch was also examined by the potentiometer method (cf. A., 1922, i, 10). The results agreed with those obtained by ultrafiltration of the starch iodide solution and analytical determination of the individual components before filtration and in the ultrafiltrate. Starch iodide is thus shown to be an adsorption product. The I_3-ion is most strongly adsorbed, the adsorption curve being normal. At the same time, the I-ion and undissociated KI and KI_3 are also adsorbed, whilst the expulsion of free iodine from the surface generally increases with increasing concentration. The determination of the partition of iodine between benzene, water, and starch (cf. von Euler and Myrbäck, A., 1922, i, 527, 1120) gave unsatisfactory results owing to the uncertainty of the partition coefficient of iodine between benzene and water. Analogous experiments using carbon tetrachloride in place of benzene give results in agreement with those quoted above, so that there is no evidence of chemical combination between the iodine and starch. Adsorbed iodine is given up again very incompletely by starch, so that the curves obtained by adjusting the equilibrium from "above" and "below" do not coincide. The actual adsorption equilibrium is, however, rapidly attained, but the starch continues to adsorb iodine owing, apparently, to a very gradual diffusion of the latter into it.
W. T. K. B.

Starch-Iodine Reaction. N. R. DHAR.—(See ii, 242.)

Topochemical Reactions. Esterification and Mercerisation of Cellulose. R. O. HERZOG and G. LONDBERG (*Ber.*, 1924, **57**, [*B*], 329—332).—Röntgen examination shows that the esterification of ramie fibre and a number of varieties of artificial silk is a normal, heterogeneous process which proceeds from exterior

to interior accompanied by solution of the cellulose esters. The progress of the reaction does not depend on the degree of arrangement of the crystallites, but on the previous chemical and physical treatment of the material. The nitration of cellulose, on the other hand, is a typical topochemical reaction occurring in the swollen fibre as in a homogeneous chemical system; denitration of cellulose nitrate under mild conditions takes place similarly.

Röntgen photographs of ramie or hemp fibres which have been mercerised without tension by sodium hydroxide solution (about 17%) and subsequently washed until free from alkali, exhibit Debye-Scherrer rings in place of the original point diagrams, showing that the crystallites have taken all possible positions. When the fibre is mercerised under such tension that the length remains unchanged, however, a point diagram is subsequently obtained, showing that the crystals lie, as originally, with the same axis in the direction of the fibre, that the crystals of mercerised cellulose have the same axial ratio and angles as the crystals of the original cellulose, and that the molecule of mercerised cellulose differs but little from that of the original cellulose, possibly to such an extent as is involved by the displacement of an oxygen linking.

H. W.

Quantitative Determination of the Fluorescent Powers (the Spectro-fluorescometry) of Cellulose and its Derivatives. S. J. Lewis (*J. Soc. Dyers and Col.*, 1924, **40**, 29—40).—The work previously described (A., 1923, ii, 334) has been extended and the methods have been improved so that the investigation of the fluorescent powers of cellulosic substances is now claimed to be easily carried out and even capable of application to industrial problems. Particularly, the spark source of ultra-violet light has been replaced by a cooled rotating tungsten arc, whereby the original feebleness of the spectrum between λ 2750—3300 and λ 2640—2730 is avoided, the necessary time for exposure has been shortened, and the method is about one thousand times more efficient, the accuracy being within 1%.

The fluorescent powers of various classes of cellulosic substances such as pure papers, pure cellulose, hydrocellulose, oxycellulose, and cellulose acetate have been determined in reference to a new standard (a specially purified paper) and the type of fluorescent curve for each class has also been determined. The previous conclusion that the fluorescent power of a cellulosic substance is independent of its physical condition has been confirmed. For instance, the fluorescent curves of cellulose acetate powder, paper, and transparent film are very similar, and the fluorescent power of oxycellulose is almost independent of its method of preparation.

Numerous curves representing the fluorescent powers of cellulose and related substances are given and discussed. A. J. H.

The Viscose Reaction. B. Rassow and M. Wadewitz (*J. pr. Chem.*, 1923, **106**, 266—332).—A study has been made of the factors affecting the viscosity of solutions of viscose (cellulose

xanthate). By the action of sodium hydroxide solutions on cellulose there appears to be formed a definite compound, having the empirical composition $C_6H_{10}O_5$,NaOH. When solutions containing less than 35% of sodium hydroxide are used, there is an equilibrium set up between cellulose, sodium hydroxide, the compound, and water. The compound is slowly decomposed by absolute ethyl alcohol. The so-called ripening of cellulose xanthate solutions, during which a fall in viscosity takes place, is probably the result of two reactions, the gradual hydrolysis of the cellulose xanthate and the disruptive action of the sodium hydroxide present on the cellulose molecular aggregates. [Cf. *B.*, 1924, 289.]

E. H. R.

Lignin. I. Flax Lignin and some Derivatives. W. J. POWELL and H. WHITTAKER (*J. Chem. Soc.*, 1924, **125**, 357—364).—Flax lignin, obtained from flax shoves by digestion with 10% sodium hydroxide solution at 130°, can be purified to a homogeneous, light brown product of the composition

$$C_{40}H_{30}O_6(OH)_5(OMe)_4\cdot CHO,$$

by pouring its solution in aqueous acetone into a large volume of dilute hydrochloric acid. Its *acetyl* derivative,

$$C_{40}H_{30}O_6(OMe)_4(OAc)_5\cdot CHO,$$

a dark brown, amorphous solid, is insoluble in cold, dilute sodium hydroxide, but is readily hydrolysed by boiling with water, indicating that the acidic properties of the lignin are to be ascribed to phenolic hydroxyl groups. By the action of methyl sulphate under very mild conditions, three methoxyl groups can be introduced into the lignin molecule, forming *methyl-lignin*,

$$C_{40}H_{32}O_8(OMe)_7\cdot CHO,$$

which is insoluble in alkali hydroxide and very resistant to hydrolysis. Attempts to acetylate the methylated product were not successful, indicating some difference between the remaining hydroxyl groups in lignin and those in its derivatives. The product of the action of hydriodic acid on the lignin agrees closely in composition with a demethylated lignin, but it cannot be acetylated, showing that reduction accompanies the demethylation. Cold, concentrated nitric acid, or a mixture of nitric and sulphuric acids, converts the lignin into a *trinitro* derivative, $C_{42}H_{39}O_{22}N_3$, a red powder which contains one methoxyl group and behaves as an aromatic nitro compound; six acetyl groups can be introduced, forming *acetylnitrolignin*. At higher temperatures, nitration is accompanied by much oxidation. The lignin reacts energetically with chlorine and bromine in absence of sunlight, with evolution of halogen acid. The products, *chlorolignin* and *bromolignin*, $C_{40}H_{20}O_8Hal_2(OMe)_2(OH)_5\cdot CHO$, are soluble in alkali hydroxides, and have suffered partial demethylation. They are not affected by hot nitric acid, and are only partly dehalogenated by boiling with sodium hydroxide solution, indicating that the remaining halogen atoms are attached to aromatic nuclei. *Acetylchlorolignin*, $C_{53}H_{42}O_{21}Cl_{12}$, and *acetylbromolignin*, $C_{42}H_{30}O_{16}Br_{12}$, as well as the

acetylnitrolignins, are readily hydrolysed. The presence of one aldehyde group in the lignin molecule is deduced from the action of Fehling's solution and of phenylhydrazine. Comparison of these results with those of Cross and Bevan, Klason (A., 1908, i, 707; 1923, i, 187), and Beckmann and Liesche (A., 1921, i, 546; 1922, i, 233), shows that the lignins from jute, flax, and pine are not identical, but that those from flax and winter rye straw are closely related.

On treatment of the neutralised washings from the lignin (see above) with calcium chloride solution, considerable quantities of the calcium salt of a substance resembling lignin, but having a much smaller methoxyl content, are obtained. From the solution of chlorolignin in cold alkali hydroxide, acids precipitate the *compound* $C_{43}H_{35}O_{16}Cl_6$. F. G. W.

Potash Fusion of Lignin, Cellulose, and Wood. E. Heuser and F. Herrmann (*Cellulosechem.*, 1924, **5**, 1—6).—The observations of Heuser and Winsvold (A., 1923, i, 541, 900) on the fusion of lignin are confirmed and extended. When iron powder is present the yield of aromatic products is increased and the elimination of carbon dioxide from the protocatechuic acid is promoted, but not to such a large extent as when the fusion is performed in an iron crucible; iron is dissolved. There is only a slightly lower yield when the fusion is carried out at 240—260° instead of 270—280°. In the presence of ammonium carbonate a portion of the pyrocatechol is re-converted into protocatechuic acid. Fusion in an atmosphere of carbon dioxide instead of hydrogen does not have this effect; an atmosphere of carbon dioxide exerts a protective influence in suppressing the formation of oxalic acid, but not so completely as hydrogen. Carbon dioxide also moderates the total reaction, presumably because it combines with the potassium hydroxide; more lignic acid remains in the product. Carbon dioxide is produced to the extent of 27—28% of the weight of lignin when the fusion is carried out in a nickel crucible in the presence of air. Since the decomposition of protocatechuic acid into pyrocatechol is only pronounced in the presence of a catalyst in an atmosphere of hydrogen, the carbon dioxide formed under normal conditions is the result of oxidation at the expense of a portion of the products of reaction. Pure pyrocatechol is substantially resistant under the conditions employed. The fusion of cellulose with potash yields no aromatic products, only oxalic acid, with 21—22% of acetic acid and 1·5—2% of formic acid. The amount of oxalic acid is not substantially altered by the use of an atmosphere of hydrogen or by adding iron as catalyst; thus its formation from cellulose is not a process of oxidation. The fusion of wood gives results exactly compatible with those described for lignin and cellulose. J. F. B.

Nature of Lignin. E. Strupp (*Cellulosechem.*, 1924, **5**, 6—7.)—The cyclo-saccharides or cycloses may be regarded as intermediate links capable of uniting partly with true carbohydrates and partly

directly with one another. The presence of hydroaromatic rings in lignin and its undetermined position between the aromatic and aliphatic systems are cited as arguments in favour of the investigation of this conception. The methyl ether of inositol is a constituent of the cambial sap of certain conifers, and from inositol are obtainable several of the aromatic and aliphatic derivatives which have been detected in the products of decomposition of lignin. J. F. B.

Transformation of Ligneous Plant Substances into Coal. I. Production of Coal-like Products from Cellulose. C. G. SCHWALBE and R. SCHEPP (*Ber.*, 1924, **57**, [*B*], 319—322).—Cellulose can be converted into coal-like substances by salts which are present in sea water at a relatively low temperature and with surprising rapidity.

Coal-like substances, the composition and nature of which have not been fully examined, are produced from wood tissue and concentrated magnesium chloride solution at 150—180°, 135°, and 95°, respectively; a similar effect is produced by zinc chloride but not by calcium chloride solutions at 135°. Since in every case hydrochloric acid is produced it remains uncertain whether the effect is to be ascribed to dehydration or to hydrolysis of cellulose to dextrose and carbonisation of the latter. H. W.

Synthesis of some New β-Amino-acids, Esters, and Alcohols. R. BRECKPOT (*Bull. Soc. chim. Belg.*, 1923, **32**, 412—433).—Using three alkyl-substituted β-aminobutyronitriles described by Bruylants (A., 1923, i, 762) as a starting-point, the author has effected their hydrolysis and the esterification of the resulting acids, and has studied the reduction of these esters and also their reactions with magnesium ethyl bromide. The following compounds are described: *β-Dimethylaminobutyric acid hydrochloride*, hygroscopic needles, obtained by the action of concentrated hydrochloric acid on β-dimethylaminobutyronitrile, *chloroplatinate*, small orange crystals, m. p. 194—195° (decomp.). *Ethyl β-dimethylaminobutyrate*, b. p. 69·5°/12 mm., 183·5—184·5°/758 mm. (partial decomp.), d_4^{20} 0·91958, n_D^{20} 1·42641, prepared by the action of dry hydrogen chloride on an alcoholic solution of the hydrochloride of the acid, when an oil, $C_9H_{17}O_4N$, b. p. 105—110°/12 mm., which could not be identified, was produced simultaneously. The ester yields a *methiodide*, colourless needles, m. p. 127—128°, and a *chloroplatinate*, flattened orange-red prisms, m. p. 178—179° (decomp.), whilst on reduction with sodium and absolute alcohol, *β-dimethylaminobutyl alcohol*, b. p. 178—180°/760 mm., d_4^{20} 0·896, n_D^{20} 1·4408, is obtained. (The hygroscopic *methiodide*, m. p. 262—263°, and the non-crystalline *hydrochloride* are described.) The ester on treatment with magnesium ethyl bromide yields a mixture of diethylpropylenecarbinol, $CHMe{:}CH{\cdot}C(OH)Et_2$, and *αα-diethyl-γ-dimethylaminobutan-α-ol*, b. p. 205—212°, d_4^{20} 0·873, n_D^{20} 1·4410 (*methiodide*, m. p. 140—142°, *hydrochloride*, a white, extremely hygroscopic solid). *β-Ethylaminobutyric acid hydrochloride*, a

crystalline mass, m. p. 72—73°, was also prepared by the action of hydrochloric acid on the corresponding nitrile; the corresponding free acid could not be prepared. *Ethyl β-ethylaminobutyrate*, b. p. 74°/12 mm., d_4^{20} 0·91549, n_D^{20} 1·42531 (*hydrochloride*, m. p. 111—114°), was obtained by passing dry hydrogen chloride through an alcoholic solution of the acid, with simultaneous production of a colourless oil, $C_{14}H_{27}O_6N$, b. p. 111—114°/19 mm. On reduction, the ester yields *β-ethylaminobutyl alcohol*, b. p. 187°, and is converted by treatment with magnesium ethyl bromide into the *lactam* of *β-ethylaminobutyric acid*, $CO<^{CH_2}_{NEt}>CHMe$, b. p. 79·5—80·5°/12·5 mm., d_4^{20} 0·9420, n_D^{20} 1·4478 (*hydrochloride*, m. p. 72—73°); a theoretical explanation of its formation is given. At the same time, an octadiene, a colourless liquid, b. p. 127—130°/761 mm., and a small quantity of hygroscopic white needles, b. p. 255—265°, which were not identified, were produced. *Ethyl β-methylaminobutyrate*, b. p. 72°/12·5 mm., was prepared in a similar manner to its homologue; with magnesium ethyl bromide it yields the *lactam* of *β-methylaminobutyric acid*, b. p. 73—74°/12 mm., together with the same octadiene mentioned above.

The author points out that the three esters described may all be obtained from allyl bromide as a starting point (cf. Bruylants, A., 1922, i, 817), and the yields at each stage are good. H. J. E.

Salting-out of Amino-acids. P. Pfeiffer and O. Angern (*Z. physiol. Chem.*, 1924, **133**, 180—192).—*l*-Tyrosine, *l*-asparagine, *d*-glutamic acid, and glycylglycine are not salted out by ammonium sulphate and sodium acetate. Glycine and sarcosine are salted out to a greater or less degree by potassium acetate, *l*-cystine by ammonium sulphate, and *dl*-alanine by potassium acetate and ammonium sulphate. *l*-Leucine, *dl*-phenylalanine, and *l*-tryptophan are precipitated by sodium chloride, potassium acetate, and ammonium sulphate. S. S. Z.

Amino-acids and Polypeptides in Combination with Neutral Salts. IV. P. Pfeiffer, M. Klossmann, and O. Angern (*Z. physiol. Chem.*, 1924, **133**, 22—61).—Compounds of glycine, alanine, sarcosine, betaine, glycylglycine, alanylglycine, and di- and tri-glycylglycine, with a number of metallic salts, mainly alkali halides, were prepared and analysed. S. S. Z.

Oxidation of Amino-acids with Hydrogen Peroxide and at the Anode. F. Fichter and F. Kuhn (*Helv. Chim. Acta*, 1924, **7**, 167—172).—The oxidation of glycine in 2*N*-sulphuric acid solution, in presence of ferrous sulphate, with hydrogen peroxide proceeds partly according to the equation, $NH_2{\cdot}CH_2{\cdot}CO_2H+3O=NH_3+2CO_2+H_2O$, but only about half the theoretical quantity of ammonia and carbon dioxide can be accounted for. When insufficient hydrogen peroxide for the above equation is used, some formic acid is produced. When the oxidation is carried out in presence of ammonia, only minute amounts of carbamide are formed. By

electrochemical oxidation of glycine in presence of ammonia, using ammonium nitrate as the electrolyte, larger quantities of carbamide are formed, and still larger quantities if ammonium carbonate is used instead of the glycine. It is concluded, therefore, that when glycine is used, the carbamide is formed from its decomposition products (cf. Fichter and Schmid, A., 1920, i, 824).

Oxidation of α-alanine with hydrogen peroxide in dilute sulphuric acid in presence of ferrous sulphate gives ammonia, acetaldehyde, acetic acid, formaldehyde, formic acid, and carbon dioxide; anodic oxidation in acid solution gives the same products. Anodic oxidation of leucine gives a mixture of *iso*valeraldehyde, *iso*valeric acid, *iso*butyric acid, acetone, acetic acid, formic acid, carbon dioxide, and ammonia. E. H. R.

Nitrogenous Components of Beetroot and Beetroot Products. E. O. VON LIPPMANN (*Ber.*, 1924, **57**, [*B*], 256—258).—An account of experiments completed in 1902.

The following substances have been isolated from the solutions obtained after removal of sugar: *d*-arginine, m. p. 207°, $[\alpha]_D^{20}$ +11·25° in aqueous solution; *d*-lysine, m. p. 193·5°, $[\alpha]_D^{20}$ +15·42° when dissolved in water; *l*-histidine, m. p. above 280° (decomp.), $[\alpha]_D^{20}$ −39·48°; proline, m. p. 203°, $[\alpha]_D^{20}$ −3·12°; scatolecarboxylic acid, m. p. 162·5°; *l*-cystine, m. p. about 260° (decomp.), $[\alpha]_D^{20}$ +221° in hydrochloric acid solution (10%). The juice of freshly-harvested but still unripe beetroot yielded *l*-phenylalanine, m. p. 263°, a substance, $C_{18}H_{20}O_5N_2$, m. p. 275°, $[\alpha]_D^{20}$ +94·15° and +38·65° in faintly acidic and alkaline solution, respectively, which is probably identical with tyrosine anhydride (A., 1922, i, 184), and a substance, $C_6H_7O_4N$, colourless prisms, m. p. 125°, probably the imide of tricarballylic acid (cf. Thole and Thorpe, T., 1911, **99**, 1688). H. W.

Deamination of Esters of Alanine and Amino*iso*butyric Acid. A. L. BARKER and G. S. SKINNER (*J. Amer. Chem. Soc.*, 1924, **46**, 403—414).—*Ethyl α-amino*iso*butyrate hydrochloride*, m. p. 155—157° (corr.), is converted by a slight excess of sodium nitrite in aqueous solution at 0° into ethyl α-methylacrylate, ethyl α-hydroxy*iso*butyrate, and a little α-methylacrylic acid. Under similar conditions, methyl α-amino*iso*butyrate hydrochloride yields very small amounts of α-methoxy*iso*butyric acid which contains a small proportion of α-hydroxy*iso*butyric acid and α-methylacrylic acid together with methyl α-methylacrylate and methyl α-hydroxy-*iso*butyrate. Methyl α-aminopropionate hydrochloride gives methyl acrylate, methyl α-chloropropionate, and methyl lactate, in addition to a non-volatile residue which is regarded as a pyrazolinedicarboxylic ester; the acidic products include α-methoxypropionic acid, lactic acid, and unsaturated and chloro acids. Ethyl α-aminopropionate hydrochloride yields ethyl acrylate, ethyl chloro- and hydroxy-propionates, ethyl diazopropionate, acrylic, lactic, α-chloropropionic, and α-ethoxypropionic acids, and certain nitrogenous residues which have not been identified. A. B. S.

Attempts to Prepare a Cyanide of Tin. J. G. F. Druce (*Chem. News*, 1924, **128**, 115—116).—No compound of tin with the cyanogen radical could be obtained by boiling an ethereal solution of stannous chloride with silver cyanide or ethyl cyanide. Freshly precipitated stannic hydroxide was dissolved in hot dilute hydrocyanic acid, and the filtered solution on evaporation in a vacuum left a pale brown, amorphous residue insoluble in water, alcohol, or ether. Analysis gave results closely agreeing with the formula $Sn(OH)_3 \cdot CN$. Lead cyanide is produced by adding an excess of potassium cyanide to a saturated solution of lead nitrate; it is a white precipitate slightly soluble in hot 5% hydrocyanic acid, from which it crystallises in colourless needles. A. R. P.

Oxidation of Saturated Hydrocarbons by Ozone. R. Koetschau and W. Flemming (*Z. angew. Chem.*, 1924, **37**, 42—44).—Saturated cyclic hydrocarbons are attacked by ozone, as is shown by a marked increase in their viscosity and refractive index. The products obtained from decahydronaphthalene are mainly of the nature of peroxides which, unlike normal ozonides, dissolve in saturated hydrocarbons. When they are treated with water, hydrogen peroxide is formed, accompanied, not by aldehydic products, but by hydroxylic and carboxylic compounds. A small proportion of decahydronaphthol was identified in the reaction products, but the constitution of the peroxides and acids is still uncertain. The oxidation is far-reaching, and is complicated by the apparent partial rupture of the ring structure, with liberation of carbon dioxide. W. T. K. B.

Benzene and the Tetrahedron Formula. C. W. A. Lely (*Chem. Weekblad*, 1924, **21**, 114—117, 117—124).—Further arguments are quoted in support of the author's triangular formula (A., 1923, i, 99, 313, 767) and criticising the arguments brought against it by Olivier, van Roon, Schoutissen, and Derx and Hermans (*ibid.*, 195, 196, 451). The conclusion is drawn that the benzene formula of Kekulé and van't Hoff's tetrahedron conception of the carbon atom no longer serve to cover all the known facts. S. I. L.

Contact Condensation of Acetylene. N. Zelinsky.—(See i, 359.)

Hydrocarbons of Kerosene. C. R. Wagner.—(See i, 357.)

Action of Nitrogen Tetroxide on Aromatic Hydrocarbons, particularly Toluene. A. Schaarschmidt and E. Smolla (*Ber.*, 1924, **57**, [*B*], 32—42).—Nitrogen tetroxide scarcely reacts with cold benzene, more readily with toluene or xylene, immediately with mesitylene with evolution of heat. A study of the interaction of the tetroxide (1 part) and the hydrocarbon (3 parts) during extended periods at the atmospheric temperature, shows that benzene gives mainly nitrobenzene, picric acid, and some dinitrobenzene. *p*-Chlorotoluene is oxidised and nitrated to *p*-chlorobenzoic acid and nitro derivatives. Xylene and mesitylene are transformed into resinous products, oxidation occurring to a

particularly marked degree in the case of mesitylene. Toluene is converted into oxalic acid (the yield of which increases greatly with prolongation of the action), benzoic acid, phenols, and benzaldehyde; the residue remaining after the product has been treated successively with water, sodium carbonate, sodium hydroxide, and sodium hydrogen sulphite consists mainly of almost equal proportions of unsaponifiable nitrotoluenes and readily hydrolysed nitrous or nitric esters of dinitrocresol. The unsaponifiable portion contains about 66% of mononitrotoluene; the remainder is a mixture of nitro products of higher boiling point, the least volatile of which decomposes explosively when heated in a vacuum at 200°. In the earlier stages of the reaction, acid, aldehydic, and neutral products are formed the weights of which are approximately in the ratio 3 : 2 : 4; when, however, the reaction is prolonged, the aldehydic components disappear almost completely in favour of the acid substances. The action depends greatly on the purity of the nitrogen tetroxide employed, and is most vigorous in the absence of water. H. W.

Reaction of Organo-Magnesium Compounds with Cupric Chloride. E. Sakellarios and T. Kyrimis (*Ber.*, 1924, **57**, [*B*], 322—326).—Diphenyl, 4 : 4′-ditolyl, 1 : 1′-dinaphthyl, and *s*-diphenylethane have been prepared by treating cupric chloride with the appropriate magnesium monoaryl halide (cf. Krizewsky and Turner, T., 1919, **115**, 559). Cupric chloride converts magnesium styryl bromide into αδ-diphenyl-$\Delta_{\alpha\gamma}$-butadiene, m. p. 147°, and magnesium *iso*amyl bromide into βη-dimethyloctane, b. p. 159—160°. Hydrodicamphene, m. p. 86°, is prepared from pinene hydrochloride. H. W.

Catalytic Effects of Zinc Chloride and Aluminium Chloride. J. F. Norris (*Ind. Eng. Chem.*, 1924, **16**, 184).—When the molecular compound of triphenylmethyl chloride and aluminium chloride is treated with ether, triphenylmethane is formed. This reaction is considered to proceed in the following way: $Ph_3C{\cdot}Cl+Et_2O=Ph_3C{\cdot}OEt+EtCl$; $Ph_3C{\cdot}OEt=Ph_3CH+MeCHO$. The first reaction is analogous to the action of aluminium chloride on a solution of benzoyl chloride in ether, the second reaction can be effected by heat alone, or in presence of aluminium chloride at the ordinary temperature. Triphenylmethane can therefore be prepared by allowing a mixture of carbon tetrachloride, benzene, and aluminium chloride to stand over-night; ether is then added, and after some hours the mixture decomposed with water. Excellent yields and a pure product are obtained. Primary alcohols are found to react readily with concentrated hydrogen chloride solution in presence of zinc chloride. This seems to indicate that the rôle of zinc chloride in reactions of this type is not that of a dehydrating agent, but of a catalyst operating by means of the formation of a molecular compound with the alcohol. C. I.

Hexaphenyl, the Linear Chain of Six Benzene Nuclei. R. Pummerer and K. Bittner (*Ber.*, 1924, **57**, [*B*], 84—88).—In continuation of previous work (A., 1922, i, 1196), 1-phenyl-

4-*p*-aminophenylbenzene is described in greater detail together with its transformation into hexaphenyl.

The preparation of 1-phenyl-4-*p*-aminophenylbenzene has been improved in many details; its success depends greatly on the purity of the reagents employed. 1-*Phenyl*-4-p-*acetamidophenylbenzene*, slender needles, m. p. 294°, 1-*phenyl*-4-p-*benzylideneaminophenylbenzene*, m. p. 262°, and the *compound*, $C_{25}H_{19}O_2N$, obtained from the base and *p*-naphthaquinone, are described. The amino compound yields a granular, yellow *diazonium sulphate* which is converted by potassium iodide into 1-*phenyl*-4-p-*iodophenylbenzene*, colourless leaflets, m. p. 247°. The action of silver powder on the iodo compound at about 330° leads to the production of *hexaphenyl*, $Ph\cdot[C_6H_4]_4\cdot Ph$, small, colourless, rhombic leaflets, m. p. 475°.

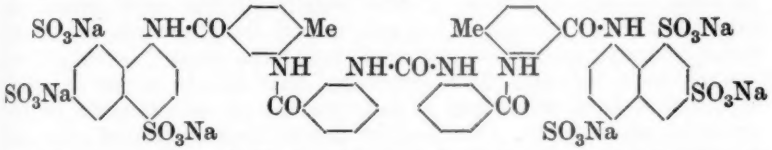
H. W.

Mechanism of the Reaction of *iso*Cyanates and *iso*Thiocyanates with the Grignard Reagent. H. GILMAN and C. R. KINNEY (*J. Amer. Chem. Soc.*, 1924, **46**, 493—497).—The reaction between phenyl *iso*cyanate and the Grignard reagent may be represented by the scheme : (I) $PhN{:}C{:}O + PhMgBr \rightarrow PhN(MgBr)\cdot C(Ph){:}O \rightarrow PhNH\cdot C(Ph)O$ or (II) $PhN{:}C{:}O + PhMgBr \rightarrow PhN{:}C(Ph)OMgBr \rightarrow PhN{:}C(Ph)OH$, the last compound undergoing rearrangement to benzanilide. To decide between the two schemes, attempts were made to displace the MgBr in the additive compound by other radicals before hydrolysis. The introduction of methyl and ethyl groups was attempted, using methyl and ethyl sulphates, but the product obtained on hydrolysis was always benzanilide. The same occurred when diphenylmethyl chloride, triphenylmethyl chloride, methyl iodide, ethyl iodide, allyl bromide, and *p*-nitrobenzyl bromide were used. As the MgBr group is more easily replaced when attached to sulphur, the *iso*thiocyanates were investigated. When the Grignard compound was treated with methyl sulphate or ethyl sulphate, the products of hydrolysis were always *S*-methylthiobenzanilide and *S*-ethylthiobenzanilide, indicating that the addition of PhMgBr had taken place, not on the $\cdot N{:}C{:}$, but on the $:C{:}S$, group, the $\cdot MgBr$ going to the sulphur. Scheme (II) represents the action in the case of the *iso*thiocyanates, and on account of the similarity of the *iso*cyanates, the same scheme probably represents the reaction in their case also.

A. B. S.

New Series of Trypanocidal Drugs. E. FOURNEAU, J. TRÉFOUËL, (MME.) J. TRÉFOUËL, and J. VALLÉE (*Compt. rend.*, 1924, **178**, 675—676).—A substance (called 309) resembling Bayer 205 in all physical and trypanocidal properties, has been prepared. It is a grey or flesh-coloured powder, very soluble in water, insoluble in alcohol, and readily hydrolysed by concentrated sulphuric acid. Whilst 20-g. mice are completely unharmed by doses of 10—12 mg., mice infected with *Trypanosoma brucei* (Nagana) are cured by doses of 0·062 mg., infection of 2 days' standing being arrested by half this quantity. The drug is prepared as follows : sodium 1-naphthylamine-4 : 6 : 8-trisulphonate is condensed, in presence of sodium

acetate, with 2-nitro-*p*-toluoyl chloride. The resulting nitro-compound is reduced, the amino compound obtained being condensed with *m*-nitrobenzoyl chloride. The product is reduced, and the amino compound formed condensed with carbonyl chloride. Bayer 205 (or the new compound, 309) is the sodium salt (following formula) of the resulting carbamide :



A large number of allied substances have been prepared, none of which has the physiological action of Bayer 205. The slightest constitutional change, *e.g.*, as obtained by using the above acid chlorides in the reverse order, is accompanied by complete suppression of trypanocidal action. E. E. T.

Compounds of the 2-Fluorenylmethyl Series. J. von Braun and H. Engel (*Ber.*, 1924, **57**, [*B*], 191—194; cf. A., 1923, i, 1087). —The cyano group of 2-cyanofluorene can be smoothly reduced to the methylamino group, without the occurrence of hydrogenation of the nucleus, by the action of hydrogen in the presence of nickel on a solution of the compound in decahydronaphthalene at 100°. 2-*Fluorenylmethylamine* and *di*-2-*fluorenylmethylamine* are thereby produced; they are separated from one another by taking advantage of the widely differing solubilities of the respective hydrochlorides in water. The primary base is a colourless, crystalline mass, m. p. 113°, b. p. 215°/10 mm.; the corresponding *hydrochloride*, m. p. 275—278° (decomp.), the *picrate*, m. p. 210°, the *acetyl* derivative, m. p. 171°, and the *phenylthiocarbamide* compound, colourless needles, m. p. 169°, are described. The secondary base, m. p. 147°, gives a *hydrochloride* which does not melt below 360° and a *nitroso* derivative, needles, m. p. 212°. Nitrous acid transforms the primary amine into 2-*fluorenylmethyl alcohol*, colourless crystals, m. p. 131°, which gives an intense bluish-green coloration with concentrated sulphuric acid; it is converted by the requisite phosphorus halide into 2-*fluorenylmethyl chloride*, m. p. 100°, and 2-*fluorenylmethyl bromide*, a pale yellow, crystalline mass, m. p. 95°. With trimethylamine, the bromide yields quantitatively 2-*fluorenylmethyltrimethylammonium bromide*, m. p. 218—219°, whilst when treated successively with hexamethylenetetramine and water, it is transformed into *fluorene*-2-*aldehyde*, colourless crystals, m. p. 174—175° (*semicarbazone*, m. p. 245—247°). 2-*Fluorenylacetonitrile*, m. p. 124°, is hydrolysed to 2-*fluorenylacetic acid*, m. p. 178°. H. W.

Kinetic Behaviour of Mixtures of Isomeric Nitrophenols on Reduction with Stannous Chloride. A. Klemenc (*Annalen*, 1924, **435**, 321—322).—The result obtained previously (this vol., i, 36) might have been due to the use of acid at only one concen-

tration. The same result is now obtained varying this concentration, of which it is therefore independent. E. E. T.

Rôle of Weight of Acyl in the Migration from Nitrogen to Oxygen. L. C. RAIFORD and C. E. GREIDER (*J. Amer. Chem. Soc.*, 1924, **46**, 430—437; cf. Raiford, A., 1920, i, 156).—To investigate the influence of the weight of the acyl group on migration from nitrogen to oxygen, mixed diacyl derivatives of the three aminophenols were prepared, using the acetyl, benzoyl, and α-naphthoyl radicals. It is concluded that weight is the deciding factor and that migration is independent of substituents in the aminophenol nucleus. The heavier group is always found attached to nitrogen. o-α-*Naphthoylamidophenyl acetate* was obtained when *o*-acetamidophenol in pyridine solution was treated with the calculated quantity of naphthoyl chloride; it forms pink crystals, m. p. 133°. o-α-*Naphthoylamidophenol* is obtained when the acetate is allowed to stand in contact with a 1% solution of potassium hydroxide for 12 hours; very fine needles, m. p. 190°. The constitution of *o*-α-naphthoylamidophenyl acetate was proved by preparing *o*-α-naphthoylamidophenol from *o*-aminophenol and acetylating it, when the same substance was obtained. 5-*Bromo*-3-*naphthoylamido*-p-*tolyl acetate* was obtained from 5-bromo-3-acetamido-*p*-cresol by the same method as above; it crystallises in needles, m. p. 218°. 5-*Bromo*-3-*naphthoylamido*-p-*cresol* forms colourless needles, m. p. 151°. 4 : 6-*Dibromo*-2-α-*naphthoylamidophenyl acetate*, from 4 : 6-dibromo-2-acetamidophenol, crystallises in colourless needles, m. p. 226°. 4 : 6-Dibromo-2-α-naphthoylamidophenol, from the acetate by leaving it in contact with 2% alkali solution for 24 hours, crystallises in needles, m. p. 175°. It was also prepared by benzoylating 4 : 6-dibromo-2-aminophenol; the product was acetylated and identified with the acetate prepared as above. o-α-*Naphthoylamidophenyl benzoate* was obtained from *o*-benzoylamidophenol by the method described above, the yield being poor; it forms colourless needles, m. p. 176°. 4 : 6-*Dibromo*-2-α-*naphthoylamidophenyl benzoate*, from 4 : 6-dibromo-2-benzoylamidophenol, by the action of α-naphthoyl chloride, crystallises poorly, m. p. 235°. Its structure was proved by benzoylating 4 : 6-dibromo-2-α-naphthoylamidophenol, when the same substance was obtained. A. B. S.

Benzoylmethylcarbinol and Acetylphenylcarbinol. K. VON AUWERS and O. JORDAN (*Biochem. Z.*, 1924, **144**, 31—43).—Benzoylmethylcarbinol has been prepared by the method of Auwers (A., 1918, i, 18), by hydrolysis of the acetyl compound with barium carbonate in water at 100°, and by hydrolysis of α-bromopropiophenone in aqueous alcohol solution with silver oxide. After purification by distillation in a vacuum, the refractive indices of the various preparations were measured, and these showed no alterations over a period of eight weeks. The purest preparation had n_D^{20} 1·5366, and was not affected by dilute acid or alkali nor by conversion to the acetyl compound and regeneration of the parent

carbinol, which is therefore concluded to be a perfectly stable compound. The observations of Neuberg and Ohle (A., 1922, i, 480, 540) on the partial interchange of benzoylmethylcarbinol (α-ketol), $Ph{\cdot}CO{\cdot}CH(OH){\cdot}CH_3$, into acetylphenylcarbinol (β-ketol), $OH{\cdot}CHPh{\cdot}COMe$, also obtained biosynthetically by the action of the enzyme carboligase (A., 1921, i, 480), are therefore not confirmed. A mixture of these two compounds (α- and β-ketols) is obtained by the oxidation of α-phenylpropylene αβ-glycol (Zincke and Zahn, A., 1910, i, 316). Attempts to prepare acetylphenylcarbinol from methylbenzylcarbinol were unsuccessful, and the products obtained from phenylacetone (Carapelle, A., 1904, i, 158) consisted chiefly of derivatives of the α-ketol. The mechanism of this reaction is discussed. Finally, attempts to obtain acetylphenylcarbinol from methylbromobenzyl ketone by the action of silver oxide yielded a product (n_D^{20} 1·5152) to which the formula $O<\begin{matrix}CHPh\\CMe{\cdot}OH\end{matrix}$ or $O<\begin{matrix}CPh{\cdot}OH\\CHMe\end{matrix}$ is ascribed, on spectrochemical grounds, and since it does not react with semicarbazide. It is suggested that the slow change of refractive index observed by Neuberg and Ohle (*loc. cit.*) in their preparations may be due to the activity of spores normally present in a biochemical and absent from a chemical laboratory (cf. Auwers and Lange, A., 1922, i, 684).

J. P.

The Presence of the Resorcinol Nucleus in the Tannin of Quebracho Wood. M. Nierenstein (*Ber.*, 1924, **57**, [*B*], 356; cf. Einbeck and Jablonski, A., 1923, i, 1099).—Resorcinol has been obtained previously by the author from quebracho tannin (A., 1906, i, 761).

H. W.

Substitution Derivatives of Aurin. C. H. Spiers (*J. Chem. Soc.*, 1924, **125**, 450—459).—Aurin is most readily isolated from corallin by saturating a solution of the latter in 60% alcohol with sulphur dioxide, and heating the precipitated compound of aurin and sulphurous acid at 130°. The aurin remaining may then be purified by fractional crystallisation from 60% alcohol. *Hexachloroaurin* is obtained as a red powder by boiling with water the product (probably hexachloroaurin sulphate) produced by the action of excess of sulphuryl chloride on aurin in glacial acetic acid solution in presence of ferric chloride. It is insoluble in the usual solvents, but crystallises from anisole in red crystals with a slight golden lustre. *Hexabromoaurin* is obtained similarly from its hydrobromide, which results from the action of excess of bromine on aurin in glacial acetic acid. It dissolves in *o*-chlorophenol, and the solution deposits the *compound* $C_{19}H_8O_3Br_6,C_6H_4Cl{\cdot}OH$ in red crystals with a brassy surface lustre. This loses *o*-chlorophenol at 120° in a vacuum, leaving pure hexabromoaurin as small, red crystals. *Hexabromodiacetylaurin*, obtained by the action of hot acetic anhydride on hexabromoaurin, and also in the cold when a trace of pyridine is present, forms yellow crystals, m. p. 280—290° (decomp.). *Hexabromotriacetylaurin*, colourless crystals of indefinite m. p.

(160—190°), is produced by the action of warm acetic anhydride on the diacetyl derivative in presence of pyridine. *Dibromoaurin* was obtained by the regulated action of bromine on a cold suspension of aurin in glacial acetic acid. It forms deep red, thin, interlocking prisms of a monohydrate, which loses water in a vacuum, leaving small, crimson crystals of the dibromoaurin. By the action of excess of iodine on a solution of aurin in sodium hydroxide, *tetraiododihydroxybenzophenone* (colourless crystals, m. p. 247°, decomp.) was the chief product, together with a little tri-iodophenol, and no iodoaurins could be isolated. *Tetraiododiacetyldihydroxybenzophenone* forms colourless crystals, m. p. 220—222°. *Trimethylaurin* was obtained by diazotising triaminotritolylmethane, and boiling the diazo compound with dilute sulphuric acid. It crystallises from a mixture of ethylene chlorohydrin and water in red crystals with a blue surface colour. *Tribromotrimethylaurin* is obtained by the action of bromine on a solution of trimethylaurin in boiling glacial acetic acid. It crystallises from ethylene chlorohydrin in reddish-brown needles with a slight golden lustre which contain 1 mol. of solvent. The latter is given up at 120° in a vacuum, leaving the tribromotrimethylaurin as small, red crystals. F. G. W.

Interaction of some Aromatic Hydrocarbons, Alcohols, and Aldehydes with Nitrogen Peroxide. L. W. Bass and T. B. Johnson (*J. Amer. Chem. Soc.*, 1924, **46**, 456—461).—Aromatic hydrocarbons show little tendency to interact with nitrogen peroxide at the ordinary temperature. Exposure to sunlight has very little effect. After heating or long exposure, there is slight evidence of nitration and oxidation. *o*-Nitrobenzaldehyde gave, besides *o*-nitrobenzoic acid, a compound which appears to be *o*-diazobenzoic acid nitrate. Benzyl alcohol was oxidised to a mixture of benzaldehyde and benzoic acid in about equal proportions. Aromatic aldehydes oxidised to acids. With *o*-, *m*-, and *p*-nitrotoluenes there was slight oxidation to *o*-, *m*-, and *p*-nitrobenzoic acids. Anthracene was partly oxidised to anthraquinone. A. B. S.

Chemical Nature of the Naphthenic Acids. I. N. Zelinsky (*Ber.*, 1924, **57**, [*B*], 42—51).—An attempt has been made to settle the vexed question of the nature of the polycyclic ring present in the naphthenic acids. The latter were converted by a series of mild reactions into hydrocarbons containing the same number of carbon atoms. These were subjected to catalytic dehydrogenation (Zelinsky, A., 1911, i, 958; 1912, i, 167) under conditions such that hexamethylene derivatives were converted into hydrogen and aromatic hydrocarbons whereas the *cyclo*butane, *cyclo*pentane, and *cyclo*heptane rings remained unaffected. It was found that the great majority of the naphthenic acids are not derivatives of *cyclo*hexane.

[With A. Tschuksanowa.]—The initial material was a series of fractions of naphthenic acids obtained from Baku petroleum. The acids were converted into their methyl esters, whereby it was found possible to isolate two fractions the analytical composition

of which accorded with that required for methyl heptanaphthenecarboxylate and methyl octanaphthenecarboxylate, respectively, but the wide range of boiling point showed them to be mixtures of isomerides. They were reduced by sodium and alcohol to the corresponding primary alcohols, octanaphthene- and nonanaphthene-alcohols, which were converted by iodine and red phosphorus into the corresponding iodides and subsequently reduced by zinc dust in the presence of aqueous alcohols to the hydrocarbons. The latter were saturated, indifferent towards permanganate and concentrated sulphuric acid, and generally similar to *cyclo*hexane and *cyclo*pentane compounds. When passed over platinum black at 300°, they yielded very little hydrogen.

The preparation of *hexahydro-o-xylene* [1 : 2-*dimethyl*cyclo*hexane*], b. p. 127·5—128°, d_{20} 0·7903, d_4^{20} 0·7893, n^{20} 1·4321, is described incidentally; the physical constants of the compound differ widely from those of octanaphthene. H. W.

Chemical Nature of the Naphthenic Acids. II. N. Zelinsky and E. Pokrowskaja (*Ber.*, 1924, **57**, [*B*], 51—58).—An investigation of the octa-, nona-, and deca-naphthenecarboxylic acids along the lines indicated in the preceding abstract. The behaviour of nona-, deca-, and undeca-naphthenes towards palladium black at 300—310° shows that they cannot contain more than small amounts of derivatives of *cyclo*hexane. H. W.

Naphthenic Acids. IV. Metallic Salts of Naphthenic Acids. Y. Tanaka, K. Horiuchi, and G. Ôyama (*J. Chem. Ind. Japan*, 1923, **26**, 1190—1203).—Pure mixed naphthenic acids derived from the waste lyes from the refining of Kurokawa petroleum were separated by distillation into three fractions consisting chiefly of trideca-, tetradeca-, and pentadeca-naphthenic acids, respectively. Metallic salts of these fractions have been prepared, and their solubilities and some other properties have been studied. The solubility increases with decreasing molecular weight of the acid. The lead salts are transparent, resinous solids, m. p. 110—118°. Manganese tridecanaphthenate is a pink powder, soluble in ether, slightly soluble in absolute alcohol (about 2% at 15°), and practically insoluble in cold or hot water. This result contradicts that of von Kozicke and von Pilat (A., 1916, i, 814). Manganese tetradecanaphthenate melts at 61—63°. The lead and manganese salts have a drying action on linseed oil. Chromium salts were obtained in two different modifications, one being a violet powder and the other a green, viscous mass; the former is changed into the latter by heating. Aluminium naphthenate forms a transparent, colourless, and porous mass which can be powdered; it has a waterproofing action. The calcium salts are white, lustrous solids and the magnesium and zinc salts white powders. K. K.

Solid Constituents of Low-temperature Coal Tar. J. Marcusson and M. Picard (*Brennstoff-Chem.*, 1924, **5**, 68—69).—The solid carboxylic acids, isolated from low-temperature coal tar, may be divided into three classes, according as they are soluble

in ether, insoluble in ether but soluble in acetone, or insoluble in ether or acetone. They are all aromatic in character and may be sulphonated and nitrated. The content of solid phenols in a tar varies with the method of distillation employed. Naphthalene or anthracene is not present in the primary tar, which contains up to 2% of solid paraffins, a considerable proportion of which is unsaturated. The acetyl value of the neutral portion of the tar both before and after hydrogenation was low, indicating that only small quantities of aldehydes and ketones were present. [Cf. *A* 1924, 287.] T. S. W.

Action of Esters on Magnesium Alkyl Halides. G. STADNIKOFF (*Ber.*, 1924, **57**, [*B*], 1—8).—An investigation of the abnormal course of the action of Grignard's reagents on esters whereby esters, ethers, and hydrocarbons are produced in addition to alcohols.

The formation of esters is attributed to the action of the iodomagnesium compounds of the alcohols, formed primarily, on the unchanged ester, thus: $2RMgI+R'\cdot CO_2Et \longrightarrow R_2R'CO\cdot MgI+EtO\cdot MgI$ and $R_2R'CO\cdot MgI+R'\cdot CO_2Et \longrightarrow R'\cdot CO_2\cdot CR_2R'+EtO\cdot MgI$. Under somewhat unusual conditions, a preparative method of obtaining the esters of complex alcohols is thereby afforded; the examples cited are benzhydryl acetate, b. p. 169—170°/11 mm., m. p. 40—42°, 3-methyl*cyclo*hexyl acetate, b. p. 187—188°/784 mm., menthyl formate, b. p. 110°/20 mm., menthyl acetate, b. p. 131°/40 mm., $[\alpha]_D$ −79·2°, menthyl benzoate, b. p. 189—190°/16 mm., m. p. 54·5—55°, *menthyl iminodiacetate*, $C_{24}H_{43}O_4N$, b. p. 263°/15 mm., m. p. 48—50°, and *menthyl cyanotriacetate*, $C_{36}H_{63}O_6N$, m. p. 80—81°. The iodomagnesium derivatives of the phenols do not react with esters.

The production of simple and mixed ethers is ascribed to the interaction of halogenomagnesium alkoxides on iodides or bromides in accordance with the scheme: $R\cdot O\cdot MgI+CHR'_2I \longrightarrow MgI_2+R\cdot O\cdot CHR'_2$, whilst the iodides are themselves formed by the action of magnesium iodide on esters of alcohols of high molecular weight as exemplified by the scheme: $R\cdot CO_2CHPh_2+MgI_2=R\cdot CO_2\cdot MgI+CHPh_2I$. The small proportion of magnesium iodide normally present in a Grignard solution is sufficient to account for the change, since the material which enters into reaction is regenerated. If this explanation be accepted, it is to be expected that hydrocarbons would be formed when an excess of magnesium is employed as indicated by the scheme: $2CHPh_2I+Mg \longrightarrow CHPh_2\cdot CHPh_2+MgI_2$. The following experimental evidence in favour of this interpretation is cited. Magnesium ethyl iodide when treated successively with benzhydrol and ethyl acetate in ethereal solution yields benzhydryl ethyl ether, b. p. 157—157·5°/14 mm., and dibenzhydryl ether, m. p. 108—109°. The same products with the addition of tetraphenylethane, m. p. 208—209°, are formed when ethyl acetate is replaced by ethyl formate; the yield of the hydrocarbon is increased by the use of an excess of magnesium. The iodomagnesium compound of triphenylcarbinol is converted

to a small extent by ethyl acetate into triphenylmethyl ethyl ether, m. p. 84—85°; the intermediate production of triphenylmethyl iodide is placed beyond doubt by the isolation of triphenylmethyl peroxide from the products of the reaction.

When, in contrast to the usual conditions, the reaction between magnesium phenyl bromide and methyl benzoate is conducted rigorously, considerable amounts of triphenylmethyl methyl ether, m. p. 83—84°, are produced in addition to triphenylcarbinol. The formation of ethers can be considerably restricted, however, by a suitable choice of radicals. Thus magnesium phenyl bromide and benzyl benzoate give only a very small proportion of *triphenylmethyl benzyl ether*, m. p. 106—107°, in boiling ethereal solution, although the yield may be increased by working under increased pressure. Magnesium phenyl bromide and ethyl benzoate give triphenylcarbinol and triphenylmethyl ethyl ether in yields of 42% and 31%, respectively, whereas ethyl formate and magnesium phenyl bromide produce dibenzhydryl ether, benzhydryl ethyl ether, and tetraphenylethane.

Ethyl formate and magnesium α-naphthyl bromide give *di-α-naphthylmethyl ethyl ether*, $C_{23}H_{20}O$, m. p. 134—135°. H. W.

Condensation of Ethyl Oxalate with Nitrotoluenes. I. *o*-Nitrotoluene. W. Wislicenus and E. Thoma (*Annalen*, 1924, **436**, 42—68).—By condensing *o*-nitrotoluene with ethyl oxalate in presence of potassium ethoxide, the authors have obtained *o*-nitrophenylpyruvic acid in a better yield (80 as against 55% of the theoretical) than resulted from Reissert's experiments (A., 1897, i, 417; 1898, i, 315). The product was first isolated as a *potassium* derivative, probably of the *aci*nitro form, $NO_2K{:}C_6H_4{:}CH{\cdot}CO{\cdot}CO_2Et$, a dark red substance. In aqueous solution, the colour gradually disappears and potassium *o*-nitrophenylpyruvate is formed. The two desmotropic forms of *o*-nitrophenylpyruvic acid were isolated. The *keto* form,

$$NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CO{\cdot}CO_2Et,$$

was obtained by decomposing the above red potassium derivative in aqueous solution and formed needles or prisms, m. p. 46—47°. The *enol* form, $NO_2{\cdot}C_6H_4{\cdot}CH{:}C(OH){\cdot}CO_2Et$, m. p. 70—71°, was produced when the decomposition was carried out in ethereal suspension. In alcoholic solution, the two forms exist together as an equilibrium mixture containing 20% of enol, as determined by titration with bromine in the usual way. *Ethyl β-bromo-o-nitrophenylpyruvate*, obtained by brominating the enol, forms white crystals melting at about 76—82°. It regenerates the parent ester when treated with sodium bisulphite, and with aqueous or alcoholic alkali is partly transformed to a *compound*, $C_{16}H_{13}O_6N_2Br$, m. p. 121—122°. *Ethyl o-nitrophenylpyruvate phenylhydrazone* forms yellow needles, m. p. 103·5°, and the *oxime*, colourless needles, m. p. 121—122°. When the ester was treated with ammonia during 4 days, *o-nitrophenylpyruvamide*, $NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CO{\cdot}CO{\cdot}NH_2$, colourless needles, m. p. 165—166°, was obtained. The ester reacts with aniline and various substituted anilines (but not with

β-naphthylamine or methylaniline) to form *anils*. Thus with aniline, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot C(:NPh) \cdot CO_2Et$, red prisms, m. p. 92°; with *p*-toluidine, dark red crystals, m. p. 90·5—91·5°; with *o*-toluidine, orange-red crystals, m. p. 77—78°; with *m*-toluidine, orange-red crystals, m. p. 138°; with 1 : 3 : 4-xylidine, red crystals, m. p. 106·5—107°; with *p*-bromoaniline, dark red prisms, m. p. 136—137°. These compounds should, however, be formulated as the tautomeric anilino-enols, as when they are brominated addition does not take place but bromine enters the nucleus (cf. Hantzsch, A., 1916, i, 12).

o-Nitrophenylpyruvic acid forms colourless leaflets, m. p. 121°. The *methyl* ester was obtained as yellow needles, sintering at 65° and melting between 83° and 87°. It appears to exist largely as the *enol* form, and the pure *keto* form was not isolated. Methylation of the ethyl ester with methyl sulphate gave exclusively *ethyl* o-*nitro*-α-*methoxycinnamate*, $NO_2 \cdot C_6H_4 \cdot CH:C(OMe) \cdot CO_2Et$, scales, m. p. 46—47°. This gave a *dibromide*,

$$NO_2 \cdot C_6H_4 \cdot CHBr \cdot CBr(OMe) \cdot CO_2Et,$$

m. p. about 98°, which by boiling with alcohol was converted into *ethyl* β-*bromo*-o-*nitro*-α-*methoxycinnamate*, colourless prisms, m. p. 79—80°. o-*Nitro*-α-*methoxycinnamic acid* itself has m. p. 160—161°; its *methyl* ester, 67·5—68°. α-*Ethoxy*-o-*nitrophenylcinnamic acid* and its *methyl* ester were obtained in a similar way, using ethyl iodide as ethylating agent, and melted at 146—147° and 49—50°, respectively. When ethyl *o*-nitrophenylpyruvate was methylated with methyl iodide, the *C*-methyl derivative, namely *ethyl* o-*nitrophenyl*-β-*methylpyruvate*, was produced. This compound is an oil and was isolated as its *phenylhydrazone*,

$$NO_2 \cdot C_6H_4 \cdot CHMe \cdot C(:N \cdot NHPh) \cdot CO_2Et,$$

white needles, m. p. 131·5—132·5°; a by-product, presumably the phenylhydrazone of the dimethyl derivative, forms yellow scales, m. p. 136°.

Ethyl *o*-nitrophenylpyruvate was benzoylated to give the O-*benzoyl* derivative, $NO_2 \cdot C_6H_4 \cdot CH:C(OBz) \cdot CO_2Et$, small tablets, m. p. 46—47°. The corresponding *acetyl* derivative forms prisms, m. p. 95—96°. When the ester is treated with benzaldehyde the *lactone*,

$$NO_2 \cdot C_6H_4 \cdot CH\text{—}CH \cdot Ph \quad | \quad >O \quad , \quad CO\text{—}CO$$

is formed, m. p. 174—176°, whilst with sodium nitrite, contrary to what Reissert has stated (*loc. cit.*), it yields *ethyl* o-*nitrophenyl*-β-*isonitrosopyruvate*,

$$NO_2 \cdot C_6H_4 \cdot C(:NOH) \cdot CO \cdot CO_2Et,$$

colourless, tetrahedral crystals, m. p. 120·5—121·5° (decomp.). It combines with diazobenzene to form a yellow *compound*. Attempts to prepare ethyl *o*-nitrophenyl-β-methylpyruvate by interaction of ethyl oxalate and *o*-nitroethylbenzene failed.

II. Condensation of Ethyl Oxalate and *p*-Nitrotoluene. [With F. Schultz.]—This reaction was carried out in the same way as that just described, but when ethyl oxalate was used there were always formed some *pp'*-dinitrostilbene and dinitrodibenzyl as by-products (cf. Reissert, *loc. cit.*). These were not produced when

methyl oxalate was used, nor from *p*-nitrotoluene and potassium or sodium ethoxide alone under the same conditions. *Ethyl* p-*nitrophenylpyruvate* forms a red *potassium* derivative resembling the *o*-isomeride described above. The free ester appears to exist solely in the enolic form as an intensely yellow substance, crystallising in rectangular prisms, m. p. 106°. The *acid* has m. p. 194° and gives a *pyridine* salt, yellowish-green needles, m. p. 150°. When the ethyl ester is reduced with tin and hydrochloric acid, it gives *p*-aminophenyl-lactic acid, m. p. 188° (Erlenmeyer, A., 1883, 994). *Ethyl* p-*nitrophenylpyruvate phenylhydrazone* forms yellowish-green prisms, m. p. 113°, and when heated with alcoholic sulphuric acid suffers intramolecular condensation, forming *ethyl* 3-p-*nitrophenylindole*-2-*carboxylate*, yellow, rectangular leaflets, m. p. 216°. The *anil* of ethyl *p*-nitrophenylpyruvate forms orange-red scales, m. p. 76°; the corresponding derivative with *o*-toluidine, orange-yellow needles, m. p. 85°; with *p*-toluidine, scarlet-red prisms, m. p. 97°; with α-naphthylamine, orange-red leaflets, m. p. 113°; with β-naphthylamine, scarlet-red, rectangular scales, m. p. 137°; with anthranilic acid, yellow needles, m. p. 194°. When the ester is treated with *o*-diamines quinoxalines are formed; thus with 1 : 3 : 4-tolylenediamine 2-*hydroxy*-3-p-*nitrobenzyl*-7-*methylquinoxaline* was obtained, m. p. 270°. With *o*-aminophenol 2-*keto*-3-p-*nitrobenzylbenzoxazine*, a deep red substance, m. p. 192°, was produced. By interaction of *p*-nitrotoluene and methyl oxalate, *methyl* p-*nitrophenylpyruvate* was prepared. This compound resembles the ethyl ester and crystallises in yellow pyramids, m. p. 149°. The β-*bromo* derivative has m. p. 114—115°, the *oxime*, 172—173°, and the *phenylhydrazone* about 136—145°.

III. Condensation of Ethyl Oxalate and 1-Nitro-2-methylnaphthalene. [With E. MUNDINGER.]—The sole product of this reaction under normal conditions was *ethyl* 1-*nitro*-2-*naphthylpyruvate*, but if double the usual quantity of potassium ethoxide were used 1 : 1′-*dinitro*-2 : 2′-*dinaphthylethane*, yellow prisms, m. p. 251°, was chiefly formed (cf. Mayer and Oppenheimer, A., 1916, i, 816). *Ethyl* 1-*nitro*-2-*naphthylpyruvate* was isolated in the two desmotropic forms. The *ketonic* form was obtained by decomposing its bisulphite compound and formed colourless needles, m. p. 84°. The *enol* was prepared by treating the potassium compound in ethereal suspension with mineral acid and separated as yellow crystals, m. p. 135°. In alcoholic solution, the two forms exist as an equilibrium mixture containing about 58% of enol. The ketonic form yields an additive *compound* with methyl alcohol, m. p. 76°. The ester forms a *copper* compound when treated with copper acetate, a brown precipitate, m. p. 182°. Its O-*benzoyl* derivative crystallised in yellow prisms, m. p. 107°; its O-*methyl* derivative in pearly prisms, m. p. 114—115°; the corresponding methoxy *acid* melts at 178°. The *anil* of ethyl nitronaphthylpyruvate forms yellow prisms, m. p. 116—117°. When the ester is treated with *o*-aminophenol an *oxazine* corresponding with the one described under II is formed (yellow prisms, m. p. 179°), and when it is reduced with zinc amalgam *ethyl* α-*naphthindolecarboxylate*

(m. p. 173—174°, free *acid*, m. p. 213°) is obtained (cf. Mayer and Oppenheimer, A., 1919, i, 17). W. A. S.

Studies in the Indene Series. I. Derivatives of Indeneglyoxylic Ester and of Indene-1-carboxylic Acid [Indene-3-carboxylic Acid]. W. Wislicenus and W. Hentrich (*Annalen*, 1924, **436**, 9—41).—Ethyl indene-1-glyoxylate,

$$CH\lessgtr^{C_6H_4}_{CH=}>CH\cdot CO\cdot CO_2Et,$$

is methylated less readily than the corresponding fluorene derivative (see p. 398) and gives a product which cannot be isolated in a pure condition and was therefore directly hydrolysed; 55% of the calculated yield of 3-methylindene (b. p. 198·5°, d_4^{20} 0·9640) was thus obtained together with tarry by-products, transference of the double bond having occurred (cf. Courtot, A., 1915, i, 392). In the same way, 3-ethylindene was prepared; yield 43% of the theoretical, b. p. 215—216° (cf. von Braun, A., 1918, i, 111). The intermediate ethyl indeneglyoxylate could not be obtained in a pure state. 1-*Benzylidene*-3-*ethylindene* crystallises in yellow, rectangular scales, m. p. 57—58°. The *benzylidene* derivative of 3-benzylindene has m. p. 137·5°; the corresponding derivative from *p*-tolualdehyde forms bundles of yellow needles, m. p. 94°, and from cinnamaldehyde orange prisms, m. p. 161—162°. *Ethyl* 3-*benzylindene*-1-*glyoxylate* forms orange, rectangular tablets, m. p. 130°. This compound, unlike its congeners, is stable. 3-*Allylindene*, b. p. 138°/27 mm., prepared by the same general method, is very easily oxidised by the air. Attempts to prepare *s*-di-indenylethane failed.

Ethyl indeneglyoxylate behaves in a similar way to the corresponding fluorene compound when treated with primary amines (cf. p. 398). The *anil*, $C_9H_7C(:NPh)\cdot CO_2Et$, forms brownish-red prisms, m. p. 142°; the *o*-toluidine derivative (unstable), dark brown prisms, m. p. 107—108°; the α-naphthylamine derivative, reddish-brown crystals, m. p. 127°. The *phenylhydrazone* forms dull yellow cubes, m. p. 69°; it decomposes when kept. The *oxime* forms a yellow, crystalline powder, m. p. 204° (decomp.).

When ethyl indeneglyoxylate reacts with one molecular proportion of hydrazine hydrate, an additive *compound* is formed to which the authors ascribe the formula $C_9H_7\cdot C(OH)(NH\cdot NH_2)\cdot CO_2Et$. This is quite stable, m. p. 184°, and decomposes when heated above its melting point. When two molecular proportions of hydrazine hydrate were used the product was the *hydrazide* of the above, m. p. 218° (decomp.). Bromination of the ester gave a definite product only when four atomic proportions of bromine were taken up, 1 : 2 : 3-*tribromohydrindene*-3-*glyoxylic acid*, white rosettes, m. p. 101°, being formed. For this reason, attempts to determine the proportion of enol in ethyl indeneglyoxylate by Meyer's bromine titration method failed.

Ethyl indeneglyoxylate reacts with diazonium compounds, giving, not a hydrazone of the hitherto unknown indenone like the corresponding fluorene derivative (Wislicenus and Densch,

A., 1902, i, 291), but a compound for which the structure $CH\leqslant\begin{matrix}C_6H_4\\CH\end{matrix}\!>\!C\!<\begin{matrix}CO\cdot CO_2Et\\N:NR\end{matrix}$ is proposed.

Ethyl 3-methylindene-1-glyoxylate gives a similar compound. This formula explains the fact that the compound dissolves readily in aqueous alkali with loss of the carbethoxy group. *Ethyl* 1-*benzeneazoindene*-1-*glyoxylate* forms dark red crystals, m. p. 146°. Similar products were obtained by interaction with *p*-nitrobenzenediazonium chloride (scarlet-red needles, m. p. 209°, decomp.), and with *m*-nitrobenzenediazonium chloride (red, amorphous powder, m. p. 201—202°, decomp.). From the latter an *acid* was obtained by dissolving it in cold dilute aqueous potassium hydroxide and reprecipitating, m. p. 151—153° (decomp.).

Indene-3-*carboxylic acid* was prepared by oxidising sodium indene-1-glyoxylate (Thiele, A., 1901, i, 76) with hydrogen peroxide (yield variable, 30—65%). The product melted at 160° and was found to be identical with that obtained by Weissgerber (A., 1911, i, 623). Transposition of the double bond has again taken place. The *hydrazide*, $C_9H_7\cdot CO\cdot NH\cdot NH_2$, forms rectangular, colourless leaflets, m. p. 186°; its *hydrochloride*, needles, darkens at 245° and decomposes at 263°. The hydrazide reacts readily with aromatic aldehydes, but not so smoothly with ketones, to give well crystallised *hydrazones*; thus with benzaldehyde, it forms white needles, m. p. 272—273°; with *o*-nitrobenzaldehyde, pale yellow needles, m. p. 215° (decomp.); with *p*-tolualdehyde, long, colourless needles, m. p. 254—255° (decomp.); with salicylaldehyde, flexible, yellow needles, m. p. 267° (decomp.); with cinnamaldehyde, sulphur-yellow leaflets, m. p. 239—242° (decomp.); with furfuraldehyde, yellow, rectangular, prismatic needles, m. p. 234°; with oxindole-3-aldehyde, yellow, clustered needles, darkening at 280°, m. p. 293° (decomp.). The *diacetyl* derivative of the hydrazide forms colourless needles, m. p. 147°; the *benzoyl* derivative, leaflets, m. p. 212—213°; a by-product, presumably the *dibenzoyl* derivative, has m. p. 253—255°. The β-*phenylhydrazide* of indene-3-carboxylic acid, $C_9H_7\cdot CO\cdot NH\cdot NHPh$, forms yellow needles, m. p. 188°. The *amide*, $C_9H_7\cdot CO\cdot NH_2$, forms yellow leaflets, m. p. 180°. The *anilide* crystallises in yellow prisms, m. p. 158°. Indene-3-carboxylic acid readily reacts with aldehydes in methylalcoholic potassium hydroxide solution to form highly coloured fulvene derivatives of the general formula, $CO_2H\cdot C\leqslant\begin{matrix}C_6H_4\\CH\end{matrix}\!>\!C:CHR$.

1-*Benzylideneindene*-3-*carboxylic acid* forms yellow needles, m. p. 222°; the 3-*furfurylidene* derivative, brownish-red, prismatic needles, m. p. 250°; the 3-*cinnamylidene* derivative is an orange powder, m. p. 235°. *Ethyl* 3-*carboxyindene*-1-*glyoxylate* forms orange-red prisms, m. p. 138·5° (decomp.). The *acid* forms a red precipitate, m. p. 199°. Its *ethyl* ester, obtained by interaction of ethyl indenecarboxylate with ethyl oxalate, crystallises in rectangular prisms, m. p. 116°. By treating the potassium derivative of potassium indene-3-carboxylate with ethyl bromide it was hoped to obtain 1-ethylindene-3-carboxylic acid, but actually

the product was mainly 3-ethylindene. The potassium compound of ethyl indenecarboxylate reacts with two molecular proportions of benzenediazonium chloride, giving an orange-red *substance*, m. p. 163°. A similar compound with *p*-nitrodiazobenzene forms a red powder, m. p. 223—225° (decomp.).

Ethyl 3-methylindene-2-carboxylate (Thiele and Rüdiger, A., 1906, i, 586) reacts with ethyl oxalate in presence of potassium ethoxide to give *ethyl* 3-*methyl*-2-*carbethoxyindene*-1-*glyoxylate*, $CO_2Et{\cdot}C_9H_5Me{\cdot}CO{\cdot}CO_2Et$, the potassium compound of which forms pearly leaflets darkening at 200° and melting with decomposition at 215°. The free ester crystallises in pale yellow needles, m. p. 123—125° (only if rapidly heated). The corresponding compound from the methyl methylindenecarboxylate forms yellow needles, m. p. 134—135°.

II. Indene-3-carboxylic Acid. [With G. MANTHE.]—Methyl indene-3-carboxylate (Weissgerber, A., 1911, i, 623) on methylation readily gave (yield 66%) *methyl* 1-*methylindene*-3-*carboxylate*, a yellow oil, b. p. 127°/14 mm., which forms an unstable *dibromide*, m. p. 87—88°, b. p. 170—185°/11 mm. When the ester was hydrolysed 3-methylindene was obtained. In the same way, *ethyl* 1-*methylindene*-3-*carboxylate* was prepared (yield 80%, b. p. 132—136°/16 mm.) and likewise hydrolysed. *Ethyl* 1-*ethylindene*-3-*carboxylate* (yield 70%, b. p. 148—150°/19 mm.) gave similarly ethylindene in 70% yield. *Ethyl* 1-*benzylindene*-3-*carboxylate* (yellow, viscous oil, b. p. 240°/20 mm.) gave a good yield (80%) of benzylindene. Attempts to prepare by this method both *s*-di-indenylethane and 1 : 1′-di-indenyl failed. When the potassium compound of ethyl indenecarboxylate was treated with one molecular proportion of benzoyl chloride, a blue compound still containing potassium was produced, whilst when an excess of benzoyl chloride was used a *dibenzoyl* derivative was formed (yellow prisms, m. p. 166°). A similar derivative was produced when *m*-nitrobenzoyl chloride was used (yellow needles, m. p. 164°). The *dibenzoyl* derivative of the methyl ester forms a yellow powder, m. p. 182°. Indene-3-carboxylic acid, but not its ethyl ester, reacts with ethyl nitrate in presence of potassium ethoxide to give *di-potassium* 1-*nitroindene*-3-*carboxylate*, $CO_2K{\cdot}C{<}\begin{matrix}C_6H_4\\CH{-}\end{matrix}{>}C{:}NO_2K$, of which the *lead* salt was also prepared.

III. 1-Nitroindene. [With K. PFEILSTICKER.]—Indene was treated with ethyl nitrate and potassium ethoxide and the hitherto unknown 1-*nitroindene* obtained as a *potassium* derivative, $CH{<}\begin{matrix}C_6H_4\\CH{-}\end{matrix}{>}C{:}NO_2K$, an unstable, yellow, crystalline substance. The free nitroindene was obtained as a crystalline, greenish-yellow precipitate, m. p. 50°, which was too easily decomposed to be recrystallised. This is the *aci*-form. It decomposes without changing over into the true nitro compound. It forms more stable condensation products with aromatic aldehydes, but not with ketones, in presence of sulphuric acid. 3-*Nitro*-1-*benzylideneindene* forms orange leaflets, m. p. 139°; 3-*nitro*-1-*tolylideneindene*,

red crystals, m. p. 105°; similar derivatives with p-*nitrobenzaldehyde* (red needles, m. p. 218—220°) and *cinnamaldehyde* (deep red crystals, decomposing at 208°) were prepared. Potassium nitroindene was converted by treatment with benzoyl chloride into 1-*nitro*-3-*benzoylindene*, yellow rhombs, m. p. 121°. The above benzylidene derivatives were reduced with tin and hydrochloric acid, giving the corresponding benzylaminoindenes. Nitroindene itself gave an unstable product. 1 : 3- (or 3 : 1-)*Benzylaminoindene* is a rapidly oxidising oil; its *hydrochloride*, microscopic crystals, m. p. 237°; its *acetyl* derivative, needles, decomposing at 243°. *Cinnamylaminoindene hydrochloride* melts at 242—245°, and its *acetyl* derivative decomposes at 267°. W. A. S.

Condensations in the Arylacetonitrile Series. I. Formyl-α-naphthylacetonitrile, Ethyl Formyl-α-naphthylacetate, and Ethyl α-Naphthyloxalacetate. W. Wislicenus, G. Butterfass, and G. Koken (*Annalen*, 1924, **436**, 69—100).—*Formyl-α-naphthylacetonitrile* was obtained by interaction of naphthylacetonitrile (Mayer and Oppenheimer, A., 1916, i, 816) and ethyl formate. The *potassium* compound forms a yellow powder. The free nitrile is an imperfectly crystalline, colourless mass, m. p. 130°, giving a brown *copper* salt. Titration with bromine indicated that from 95·8 to 99·7% (in different preparations) existed in the enolic form. It should therefore be formulated as hydroxymethylenenaphthylacetonitrile, $C_{10}H_7 \cdot C(CN) \cdot CH \cdot OH$ (cf. Wislicenus, A., 1896, i, 522). It forms an *anilide*, white leaflets, m. p. 152—154°; p-*toluidide*, prisms, m. p. 142°; *semicarbazide*, diamond-shaped scales, m. p. 172—173°; and *hydroxylamide*, needles, m. p. 111°. It reacts with phenyl*iso*cyanate only at a much higher temperature than similar compounds (cf. Wislicenus, *loc. cit.*) to form the *carbanilate*, $NHPh \cdot CO \cdot O \cdot CH \cdot C(C_{10}H_7) \cdot CN$, pale yellow needles, m. p. 158—159° (decomp.).

Various derivatives of ethyl formyl-α-naphthylacetate (Wislicenus and Elvert, A., 1917, i, 202) which could not be obtained directly by simultaneous hydrolysis and esterification of the nitrile, were prepared. The *anilide* forms quadratic prisms, m. p. 94—96°; the p-*toluidide*, glistening crystals, m. p. 90—91°. The latter derivative when heated at 250—260° suffered intramolecular condensation and 3-α-*naphthyl*-4-*hydroxy*-6-*methylquinoline* was formed (needles, m. p. 302—305°, subliming at a somewhat higher temperature; *picrate*, m. p. 140—145°). When ethyl formylnaphthylacetate was reduced by Clemmensen's method, it gave a mixture of α-(α-*naphthyl*)*hydracrylic acid* (crystalline powder, m. p. 112°) and *ethyl* α-*naphthylacrylate* (an oil, b. p. 220—230°/12 mm.). α-*Naphthylacrylic acid* forms needles, m. p. 152—154°. Ethyl formyl-α-naphthylacetate was alkylated and found to give invariably *O*-derivatives. The *methyl* derivative formed an indefinitely crystalline mass, m. p. 63—64°, and the *ethyl* derivative needles, m. p. 75°.

Ethyl α-naphthylacetate and ethyl oxalate were condensed together in the usual way to produce *ethyl* α-*naphthyloxalacetate*,

$C_{10}H_7 \cdot CH(CO_2Et) \cdot CO \cdot CO_2Et$, a yellow oil which decomposes when distilled. Its *potassium* salt forms silky leaflets which decompose at 220—223°; its *copper* salt has a m. p. dependent on the solvent from which it is recrystallised. With phenylhydrazine, *ethyl 1-phenyl-4-α-naphthyl-5-pyrazolone-3-carboxylate* is obtained as microscopic leaflets, m. p. 213—214°. When the ester is heated at 180—186° it loses carbon monoxide, forming *ethyl α-naphthylmalonate* (clustered prisms, m. p. 59—60°), the sodium derivative of which, by interaction with ethyl bromoacetate and subsequent hydrolysis, gives *α-naphthylsuccinic acid*, rectangular scales, m. p. 206° (decomp.).

II. Formyl-β-naphthylacetonitrile and Ethyl Formyl-β-naphthylacetate. [With H. RIETHMÜLLER.]—The β-naphthyl derivative resembles the α-isomeride described above. It crystallises in leaflets, m. p. 181—182°, gives a brown *copper* salt, and appears to exist mainly in the *enolic* form. Its *O-benzoyl* derivative forms needles, m. p. 188°; the *anilide*, yellow needles, m. p. 185°; *p-toluidide*, yellowish-green leaflets and needles, m. p. 199—201°; *oxime*, leaflets, m. p. 135—136°; compound with *phenylcarbimide*, needles, m. p. 178° (decomp.). It reacts with benzenediazonium chloride to form *β-naphthylglyoxylonitrile phenylhydrazone* (yellow needles, m. p. 195—196°), the formyl group being displaced. When formyl-β-naphthylacetonitrile is treated with bromine, an impure *bromo* derivative, m. p. 162—164°, is obtained, whilst with iodine its potassium compound in methyl-alcoholic solution gives *s-di-β-naphthylsuccinonitrile*, $C_{10}H_7 \cdot CH(CN) \cdot CH(CN) \cdot C_{10}H_7$, colourless prisms, m. p. 246—249°. The free nitrile in aqueous methyl alcohol with iodine and sodium hydroxide gives *s-di-β-naphthyldicyanoethylene*, $C_{10}H_7 \cdot C(CN) : C(CN) \cdot C_{10}H_7$, yellow needles, m. p. 204°. The latter compound was also obtained by treating β-naphthylacetonitrile in a similar way.

Ethyl formyl-β-naphthylacetate gave on reduction and hydrolysis the corresponding *α-(β-naphthyl)-β-hydroxypropionic acid*, $OH \cdot CH_2 \cdot CH(C_{10}H_7) \cdot CO_2H$, which formed clustered crystals, m. p. 154—156°. Ethyl formyl-β-naphthylacetate gives an *anilide*, yellow needles, m. p. 91—92°; with phenylhydrazine it forms, not the expected phenylhydrazone, but *1-phenyl-4-β-naphthyl-5-pyrazolone*, colourless needles, m. p. 219—220°, yet with 2 : 4-*dinitrophenylhydrazine* the second reaction does not take place and the corresponding *dinitrophenylhydrazone* only is formed, orange-yellow crystals, sintering at 110° and melting between 115° and 118°.

III. Ester Condensations with Benzyl Cyanide. [With H. EICHERT and M. MARQUARDT.]—Cyanodeoxybenzoin,

$$C_6H_5 \cdot CO \cdot CH(CN) \cdot C_6H_5,$$

was obtained by interaction of ethyl benzoate, benzyl cyanide, and metallic potassium in yields superior to those of earlier workers (Walther and Schickler, A., 1897, i, 522; Bodroux, A., 1911, i, 545). It forms colourless scales, m. p. 91—92°, and gives an *anil*, yellow needles, m. p. 201°. By simultaneous hydrolysis and esterification *ethyl benzoylphenylacetate* (needles, m. p. 90—91°; b. p. 220—225°/

13 mm.) and the corresponding *methyl* ester (rosettes of colourless prisms, m. p. 74—75°) were obtained. Both compounds exist in solution in the two desmotropic forms; in the case of the *methyl* ester, the enolic form accounts for 4—5% of the whole. Ethyl benzoylphenylacetate heated with aniline forms *benzoylphenylacetanilide*, Bz·CHPh·CO·NHPh, colourless needles, m. p. 168°; with phenylhydrazine it gives either the *phenylhydrazone* (needles, m. p. 173—174°) or, at a higher temperature, 1 : 3 : 4-*triphenyl*-5-*pyrazolone*, leaflets, m. p. 193—194°. When it was treated with phosphorus pentachloride, a mixture of 3-*chloro*-2-*phenylindone*, $CCl\langle\begin{smallmatrix}C_6H_4\\CPh\end{smallmatrix}\rangle CO$, orange-red needles, m. p. 93—94°, b. p. 205—210°/13 mm., and *ethyl chlorobenzoylphenylacetate*, needles, m. p. 44—45°, b. p. 225—230°/12 mm., was formed. The latter compound was also obtained by direct chlorination of the ester.

Ethyl benzoylbenzoate (A., 1908, i, 994) was similarly condensed with benzyl cyanide to form *benzoylbenzoylphenylacetonitrile*, crystallising from alcohol in colourless needles or scales, m. p. 214°, and from benzene in irregular crystals, m. p. 188°. Neither is the enolic form. The compound resists hydrolysis, and forms a loose compound with hydrogen chloride. It is unaffected by hydrazine, aniline, and the like, and the only derivative obtained was *benzoylbenzoylphenylmethylacetonitrile*, $Bz\cdot C_6H_4\cdot CO\cdot CMePh\cdot CN$, prisms, m. p. 145°.

Ethyl *iso*butyrate and benzyl cyanide condensed to form *phenyl*-iso*butyroacetonitrile* (β-*keto*-α-*phenyl*-γ-*methylvaleronitrile*), $CHMe_2\cdot CO\cdot CHPh\cdot CN$, a yellow oil, b. p. 154—156°/13 mm. The *bromo* derivative (needles, m. p. 192°), *phenylhydrazone* (needles, m. p. 109°), *hydrazone* (needles, m. p. 102°), *oxime* (needles, m. p. 85°), and *semicarbazone* (needles, m. p. 147°) were prepared. By simultaneous hydrolysis and esterification, *ethyl* α-*phenyl*iso*butyroacetate* (oil, b. p. 150—160°/13 mm.) and the corresponding *methyl* ester (leaflets, m. p. 52°) were obtained. The *acid*, $CHMe_2\cdot CO\cdot CHPh\cdot CO_2H$, forms colourless needles, m. p. 159°. From the ester with phenylhydrazine 1 : 4-*diphenyl*-3-iso*propylpyrazolone* (colourless needles, m. p. 191°) and with hydrazine 4-*phenyl*-3-iso*propylpyrazolone* (m. p. 192°) were obtained, whilst with semicarbazide, 4-*phenyl*-3-iso*propyl*-5-*pyrazolone*-1-*carboxylamide*, $\begin{smallmatrix}Pr^{\beta}C{:}N\text{—}N\cdot CONH_2\\ \quad\quad\quad\

Fluorene- and 2-Nitrofluorene-9-glyoxylic Esters. W. WISLICENUS and H. WEITEMEYER (*Annalen*, 1924, **436**, 1—9).—*Fluorene-9-glycollic acid*, which the authors (A., 1921, i, 511) failed to obtain from its ester, prepared by reducing ethyl fluorene-9-glyoxylate with aluminium amalgam, owing to simultaneous dehydration to dibenzofulvene-ω-carboxylic acid, is produced directly when the reduction is carried out by Clemmensen's method. *Methyl fluorene-9-glycollate* forms white needles, m. p. 96°. When ethyl fluorene-9-glyoxylate or the free acid is oxidised with hydrogen peroxide following Reissert's procedure, it gives, not the expected fluorene-9-carboxylic acid, but exclusively fluorenone. The product obtained by Wislicenus and Densch (A., 1902, i, 291) by methylating ethyl fluoreneglyoxylate is the *C*-methyl derivative, as it may be easily hydrolysed to 9-methylfluorene. Ethyl fluoreneglyoxylate may be nitrated: the glyoxylyl group is displaced and 2 : 9-*dinitrofluorene* formed. This substance crystallises in white needles which turn yellow on exposure to light, m. p. 136°. It decomposed when heated above its melting point, giving 2-nitrofluorene. The same compound was obtained, and its constitution proved, by further nitrating both 9-nitrofluorene (Wislicenus and Waldmuller, A., 1908, i, 973) and ethyl 2-nitrofluorene-9-glyoxylate. Although 9-nitrofluorene reacts with alcoholic potassium hydroxide, the 2 : 9-dinitro derivative is insoluble in this reagent and is unable to pass over into an *aci*-form. Ethyl fluorene-9-glyoxylate yields an *anil*, $C_{13}H_9{\cdot}C(:NPh){\cdot}CO_2Et$, orange-yellow crystals, m. p. 137°, and corresponding derivatives with *p*-toluidine and β-naphthylamine (m. p. 156°). With hydrazine, on the other hand, the ethoxy group is displaced and a *hydrazide* formed, $C_{13}H_9{\cdot}CO{\cdot}CO{\cdot}NH{\cdot}NH_2$, small, yellow crystals, m. p. above 350°. This compound reacts with benzaldehyde to form a *benzylidene* derivative, crystallising in needles which decompose above 350°, and with acetone to give the *hydrazone*, $C_{13}H_9{\cdot}CO{\cdot}CO{\cdot}NH{\cdot}N{:}CMe_2$, m. p. 216°.

In 2-nitrofluorene, as in 2 : 7-dibromofluorene (Sieglitz, A., 1920, i, 605), the methylene group is more reactive than in fluorene itself. Thus when a warm solution of 2-nitrofluorene in benzene is added to a mixture of ethyl oxalate and potassium ethoxide, the potassium salt of 2-nitrofluorene-9-glyoxylic ester is immediately thrown down. *Ethyl 2-nitrofluorene-9-glyoxylate* forms yellow crystals, m. p. 143°. It gives coloured precipitates with heavy metals. The ester must be hydrolysed at temperatures below 80°, otherwise scission takes place and 2-nitrofluorene is reproduced. The free acid, $NO_2{\cdot}C_{13}H_8{\cdot}CO{\cdot}CO_2H,H_2O$, forms minute yellow crystals, m. p. 183°. The *methyl* ester has an indefinite melting point, about 120°. The ethyl ester yields a *phenylhydrazone*, yellowish-brown crystals, m. p. 192°; an *anil*, dark red crystals, m. p. 162°, and corresponding derivatives with *p*-toluidine and β-naphthylamine, m. p. 164° and 187°, respectively. Like the unsubstituted fluoreneglyoxylic ester, it gives a *benzoyl* derivative, $NO_2{\cdot}C_{13}H_7{:}C(OBz){\cdot}CO_2Et$ (cf. Wislicenus and Densch, *loc. cit.*), minute yellow crystals, m. p. 137—138°, easily decomposed again by solution in alcoholic potassium hydroxide. W. A. S.

Equilibrium in the System, Sodium Phthalate–Sodium Sulphate–Water. H. W. Foote and S. B. Smith (*J. Amer. Chem. Soc.*, 1924, **46**, 84—88).—The solubility relations of the system, sodium phthalate–sodium sulphate–water have been determined at 0°, 25°, and 35°. The transition temperature at the quintuple point, where the solid phases are anhydrous sodium sulphate, the decahydrate of sodium sulphate, and hydrated sodium phthalate, has been found to be 23°. When crystallised from water at the ordinary temperature, sodium phthalate has the composition represented by $2Na_2C_8H_4O_4,7H_2O$. J. F. S.

Unsaturated Lactones. S. Gabriel, L. Kornfeld, and C. Grunert (*Ber.*, 1924, **57**, [*B*], 302—306).—An investigation of the behaviour of arylidene- and alkylidenephthalides containing a bromine atom in the side chain towards sodium methoxide.

α-Bromobenzylidenephthalide, $CO<\overset{C_6H_4}{O}>C{:}CBr\cdot Ph$, quadratic leaflets, m. p. 193°, is obtained by heating the corresponding dibromide in a current of carbon dioxide at 140—150° until hydrogen bromide ceases to be evolved. It is transformed by a solution of sodium in methyl alcohol into *hydroxydiketophenylhydrindene*, $C_6H_4<\overset{CO}{CO}>C(OH)Ph$, yellow needles, m. p. 192° (in a vacuum), which, when dissolved in alkali hydroxide and exposed to the air, passes into *benzil-o-carboxylic acid*, $COPh\cdot CO\cdot C_6H_4\cdot CO_2H$, m. p. 140—141°. *Methoxydiketophenylhydrindene* crystallises in needles, m. p. 114°. α-Bromobenzylidenephthalide is not appreciably affected by boiling water, but is transformed by boiling potassium hydroxide solution (20%) into benzhydroldicarboxylic acid, $CO_2H\cdot C_6H_4\cdot CPh(OH)\cdot CO_2H$.

α-Bromo-*p*-tolylidenephthalide is converted in a similar manner into *4′-methylbenzil-2-carboxylic acid*, small needles, m. p. 143°.

α-Bromopropiophenone-o-carboxylic acid,

$$CO_2H\cdot C_6H_4\cdot CO\cdot CHBrMe,$$

needles, m. p. 110°, is transformed by potassium hydroxide into *hydroxydiketomethylhydrindene*, which readily becomes oxidised on exposure to air and by a saturated solution of hydrogen bromide in glacial acetic acid to the *dibromo* compound,

$$CO<\overset{C_6H_4}{O}>CBr\cdot CHBr\cdot CH_3,$$

rhombic crystals, m. p. 97—99°. *αα-Dibromopropiophenone-o-carboxylic acid*, needles, m. p. 140°, when treated successively with boiling water and phenylhydrazine, gives a *phenylhydrazone*, $CO_2H\cdot C_6H_4\cdot CO\cdot C(:N\cdot NHPh)\cdot Me$, or $CO_2H\cdot C_6H_4\cdot C(:N\cdot NHPh)\cdot CO\cdot Me$, quadratic plates, m. p. 219° (decomp.).

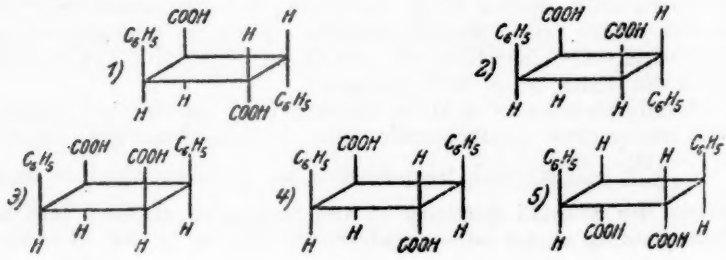
Phthalylideneacetic acid is converted by phosphoryl chloride and phosphorus pentachloride into *phthalylideneacetyl chloride*, $CO<\overset{C_6H_4}{O}>C{:}CH\cdot COCl$, long needles, m. p. 158°, which is transformed by a small quantity of the respective alcohols into the corresponding *methyl* ester, quadratic leaflets, m. p. 168° (decomp.),

and *ethyl* ester, m. p. 132—134°; when boiled with an excess of the alcohols, however, it yields *methyl* o-*carboxybenzoylacetate*, $CO_2Me{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2{\cdot}CO_2Me$, m. p. 73°, or the corresponding *ethyl* ester. *Methyl diketohydrindenecarboxylate*, $C_6H_4\langle\begin{matrix}CO\\CO\end{matrix}\rangle CH{\cdot}CO_2Me$, is prepared by the action of potassium hydroxide solution at 0° on the dimethyl ester or of sodium methoxide on methyl phthalylideneacetate. The diethyl ester is converted similarly into ethyl diketohydrindenecarboxylate, m. p. 76°. H. W.

Fluorene Series. VIII. Synthesis of Fluorenone-1-carboxylic Acid. A. Sieglitz (*Ber.*, 1924, **57**, [*B*], 316—317).—2′-Aminobenzophenone-2-carboxylic acid is diazotised in sulphuric acid solution and the diazonium solution is warmed, thus giving anthraquinone, fluorenone, and fluorenone-1-carboxylic acid, m. p. 192—193° (cf. Mayer and Freitag, A., 1921, i, 248); the main product of the change, however, is 2′-*hydroxybenzophenone*-2-*carboxylic acid*, colourless needles, m. p. 170—171°, which is converted by methyl sulphate and potassium hydroxide into 2′-*methoxybenzophenone*-2-*carboxylic acid*, colourless crystals, m. p. 144—145°, and by concentrated sulphuric acid into 1-hydroxyanthraquinone, m. p. 191°. H. W.

Synthesis of Depsides of *iso*Ferulic Acid [3-Hydroxy-4-methoxycinnamic Acid]. F. Mauthner (*J. pr. Chem.*, 1923, **106**, 333—335; cf. A., 1922, i, 936).—*Carbomethoxy*iso*ferulic acid*, obtained by the action of methyl chlorocarbonate on *iso*ferulic acid in alkaline solution, forms crystals, m. p. 223—224° (decomp.). It is converted by phosphorus pentachloride into *carbomethoxy*iso*ferulyl chloride*, colourless needles, m. p. 84°. With *p*-hydroxybenzoic acid, this gives p-*carbomethoxy*iso*ferulyloxybenzoic acid*, colourless crystals, m. p. 206—207°. The carbomethoxy group is removed by the slow action of ammonia in pyridine solution. The depside, p-iso*ferulyloxybenzoic acid*, forms colourless crystals, m. p. 217—218°. m-*Carbomethoxy*iso*ferulyloxybenzoic acid* forms colourless crystals, m. p. 203—204°, and m-iso*ferulyloxybenzoic acid*, colourless crystals, m. p. 191—192°. E. H. R.

Stereoisomerism of the Truxillic Acids and the Discovery of the Remaining Acid of this Group. VIII. R. Stoermer and F. Bacher (*Ber.*, 1924, **57**, [*B*], 15—23).—Theoretically five truxillic acids should exist, the configurations of which are shown by the formulæ :



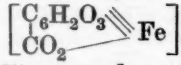
The configurations 1 and 2 have been assigned definitely to α- and γ-truxillic acids respectively (cf. A., 1923, i, 929). ε-Truxillic acid is characterised as a *cis*-compound since it yields a unimolecular, crystalline imide from which it is smoothly regenerated. The *cis*-nature of η-truxillic acid follows from its ready conversion into the anhydride (cf. Stobbe and Zschoch, A., 1923, i, 337); since it is shown that the heavy groups lie on the same side of the *cyclo*butane ring, it is proposed to designate the compound *peri*-truxillic acid (configuration 3). The action of hydrochloric acid at 180° or of an excess of boiling sodium hydroxide on the *peri*-acid yields the outstanding member of the group, which is termed *epi*-truxillic acid owing to its production by a type of epimeric change. The conversion of the *epi*-acid by acetic anhydride into ε-truxillic acid (5) shows it to be a *trans*-compound to which the constitution 4 must necessarily be assigned.

The following individual compounds are described: *peri*-truxillic anhydride, prepared by a modification of the method of Stobbe and Zschoch (*loc. cit.*), m. p. 285°; *peri*-truxillic acid, m. p. 266° (decomp.) (Stobbe and Zschoch give m. p. 280°); *methyl* peri-*truxillate*, obtained by treatment of the acid with an ethereal solution of diazomethane or by the rapid action of methyl sulphate and alkali hydroxide, colourless crystals, m. p. 104—105°; *methyl hydrogen* peri-*truxillate*, from the anhydride and methyl alcohol at 180—200°, m. p. 192°; peri-(? epi-)*truxillamic acid*, small, quadratic plates or needles, m. p. 264° (decomp.); peri-*truxillanilic acid*, m. p. 247° (decomp.), from the *peri*-anhydride and boiling aniline whereby ε-truxilldianilide, m. p. 283°, is also produced; *methyl* peri-*truxillanilate*, m. p. 131°; *methyl* ε-*truxillanilate*, m. p. 159°; epi-*truxillic acid*, prepared most conveniently by heating the *peri*-acid with an excess of sodium hydroxide solution (10%), m. p. 285—287° (with transformation into ε-truxillic acid); *methyl* epi-*truxillate*, from the acid by means of diazomethane, methyl sulphate, or methyl-alcoholic hydrogen chloride, m. p. 111—112°; *methyl hydrogen* epi-*truxillate*, prepared by the partial hydrolysis of the normal ester with alcoholic potassium hydroxide solution, m. p. 204·5°. *epi*-Truxillic acid is converted by aniline at 190—210° into ε-truxilldianilide, and, apparently, a mixture of the two theoretically possible *epi*-truxillanilic acids which has not been separated satisfactorily into its components. H. W.

Formation and Ageing of Written Characters. The Primary Ink-salts of Iron Inks. F. Zetzsche, G. Vieli, G. Liljeqvist, and A. Loosli (*Annalen*, 1924, **435**, 233—264).—The primary ink salts have been prepared by the following method: the parent hydroxy compound (*e.g.*, salicylic acid) was treated with the theoretical quantity (see below) of a solution of ferrous sulphate in dilute sulphuric acid, the mixture neutralised with sodium hydroxide, and then shaken in an atmosphere of oxygen and carbon dioxide, until no more oxygen was absorbed. In the case of hydroxy compounds which are readily oxidised in alkaline solution (*e.g.*, pyrogallol), neutralisation was effected in the above

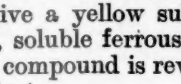
oxygen–carbon dioxide atmosphere. In this manner, the formation of the ink salts can be followed and controlled, and that of secondary (oxidation) products avoided. The experimental procedure adopted follows very closely the mechanism of the formation of written characters.

Gallic acid gives rise to *monogallatoferric* acid,

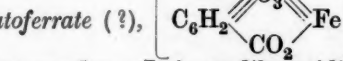


$$H,3H_2O,$$

a violet, microcrystalline powder, affording gallic acid on being treated with acids, dissolving in alkali to a blue, red, or yellow solution, according to the concentration, the latter solution being oxidised by air to give a yellow substance (galloflavine ?). The conversion of yellow, soluble ferrous gallate, $(C_6H_2[OH]_3{\cdot}CO_2)_2Fe$, into the above violet compound is reversed in presence of hydrogen and a platinum catalyst.

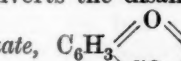
Using a greater proportion of ferrous sulphate to gallic acid, *ferric monogallatoferrate* (?),  $Fe,12H_2O$, results, as a bluish-violet powder. It is readily oxidised, gives ferric oxide on heating at 85—90° and ferric hydroxide on treating with alkali.

Ferric disalicylate (*disalicylatoferric acid*),



$$H,3H_2O,$$

red needles, gives a bluish-red solution in hot water, carbon dioxide being evolved on boiling. Unless care is taken in the preparation of this compound, Weinland's hexasalicylatotriferridisalicylatoferrate (cf. A., 1917, i, 649, and previous papers) is obtained. Alkali converts the disalicylate into alkali di- and trisalicylatoferrates.

Ferric protocatechuate,  $Fe,3H_2O$, is a violet-blue, microcrystalline powder. The *ferric* salt of gallamide,

$$NH_2{\cdot}CO{\cdot}C_6H_2{:}O_3{:}Fe,2{\cdot}5H_2O,$$

is a dark blue, microcrystalline powder; the *ferric* salt of gallanilide, $NHPh{\cdot}CO{\cdot}C_6H_2{:}O_3{:}Fe,3H_2O$, a dark violet powder and the *ferric* salt of ethyl gallate, $CO_2Et{\cdot}C_6H_2{:}O_3{:}Fe,2H_2O$, a dark blue powder. The last four compounds give wine-red solutions in aqueous alkali.

The *ferric* salt of tribromopyrogallol, $C_6Br_3{:}O_3{:}Fe,2H_2O$, is a dark blue powder, rapidly becoming brown owing to decomposition. The *diferric* salt of digalloylethyleneglycol,

$$\begin{matrix} CH_2{\cdot}O{\cdot}CO{\cdot}C_6H_2{:}O_3{:}Fe,2H_2O \\ | \\ CH_2{\cdot}O{\cdot}CO{\cdot}C_6H_2{:}O_3{:}Fe,2H_2O' \end{matrix}$$

is a bluish-violet powder, and the *triferric* salt of trigalloylglycerol, $C_{24}H_{11}O_{15}Fe_3,2H_2O$ (having a constitution similar to that of the glycol derivative) a bluish-violet powder, affording a red solution with alkali. The *pentaferric* salt of pentagalloyl-β-glucose, $C_{41}H_{37}O_{36}Fe_5,10H_2O$, and *pentaferritannate*, $C_{76}H_{37}O_{46}Fe_5,10H_2O$, have similar properties.

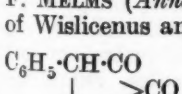
The proportions of phenolic compound to iron (mols. of phenolic compound : atoms of iron) in other primary ferric ink salts (which have not been actually isolated) are as follows: pyrocatechol (violet, 2 : 1), protocatechuic aldehyde (violet, 2 : 1), β-resorcylic acid (reddish-yellow, 1 : 1), gentisic acid (violet-red, 1 : 1), dibromopyrogallol (blue, 1 : 1), dibromogallic acid (dark blue, 1 : 1), and pyrogallolcarboxylic acid (dark violet, 1 : 1).

When ink is applied to paper, neutralisation of the acid present occurs first, followed by atmospheric oxidation of the ferrous salts, which are converted into bluish-violet insoluble primary ink salts (*e.g.*, of the gallic acid type). By the further action of atmospheric oxygen and moisture, the primary salts undergo oxidation, carboxyl or carbethoxyl groups being removed, with formation of carbon dioxide and brown secondary ink salts (*e.g.*, of the pyrogallol type). The black shade acquired by writing ink a week or so after use is due to the presence of a mixture of primary and secondary salts, or, in the case of salts rich in iron, to the presence, also, of ferric hydroxide. The addition of gum arabic to inks hinders atmospheric oxidation and loss of carbon dioxide.

Complete oxidation to the secondary ink salt type takes, on the average, twenty or thirty years. After a much longer time, ferric oxide or hydroxide alone will remain on the paper. E. E. T.

o-Cresoltetrachlorophthalein and some of its Derivatives. E. L. Arnold (*J. Amer. Chem. Soc.*, 1924, **46**, 489—493).—o-*Cresoltetrachlorophthalein* was prepared by condensing tetrachlorophthalic acid with *o*-cresol, using stannic chloride. It forms colourless crystals, m. p. 292—293° (decomp.). It resembles phenolphthalein and phenoltetrachlorophthalein, acting as an indicator, purple in alkaline solution; the end-point is between p_H 8·5 and 9. It forms a colourless *diacetyl* derivative, m. p. 207—208°, and a *dimethyl ether*, m. p. 212—213°. In concentrated sulphuric acid it gives a red solution probably due to sulphate formation. The spectrum of *o*-cresoltetrachlorophthalein in absolute ethyl alcohol is very similar to that of phenoltetrachlorophthalein, showing four weak bands in the ultra-violet, whereas that of phenolphthalein has only two bands, which correspond with the more prominent bands of the other two spectra. These bands are of frequency 3523 and 3613. A. B. S.

Ring Syntheses with Ethyl Oxalate. W. Wislicenus and F. Melms (*Annalen*, 1924, **436**, 101—112).—Continuing the work of Wislicenus and Schollkopf (A., 1917, i, 700), *ethyl triketophenylcyclopentaneglyoxylate* (annexed formula), was prepared by interaction of benzyl methyl ketone and ethyl oxalate (2 mols.) in presence of potassium ethoxide. This substance (yellow needles, m. p. 169—170°) is strongly enolised. It forms a red *di-potassium* salt and a dark red *copper* salt. The *acid* was obtained by mild alkaline hydrolysis as an orange powder, m. p. 214° (decomp.). When the ester was subjected to acid hydrolysis,



scission took place and 2 : 4 : 5-*triketo*-1-*phenyl*cyclo*pentane* was formed, crystallising from benzene in yellow needles, from alcohol in colourless needles, whilst an orange modification was obtained when the compound was fused and again cooled, or boiled with water. All three forms melted at 167°. An aqueous solution of the substance is strongly acid to litmus and reduces Fehling's solution. The *phenylhydrazone* (only one keto group enters into these reactions) forms greenish-yellow scales, m. p. 241°, the *anil* orange-red scales, m. p. 172°, the p-*toluidine* derivative, red crystals, m. p. 195—196°. The *quinoxaline* formed by interaction with *o*-phenylenediamine forms brown needles, m. p. 251°. The methyl ether, 2 : 4-*diketo*-5-*methoxy*-1-*phenyl*cyclo*pentene*, in preparing which diazomethane was used, forms colourless crystals, m. p. 54—55°. The *benzylidene* derivative of triketophenyl*cyclo*pentane forms yellow crystals, m. p. 219°; similar derivatives with *p*-tolualdehyde (m. p. 206—207°) and *p*-nitrobenzaldehyde (m. p. 262—264°) were prepared; the latter is noteworthy in that the colour of the solution varies with the solvent employed. The *dibromo* derivative has m. p. 185°. When triketophenyl*cyclo*pentane was dissolved in alkali and reprecipitated, it was found to have been converted apparently into a *bis*-product of high melting point. A preliminary investigation of the condensations of ethyl β-ethoxyglutaconate, ethyl acetonedicarboxylate, and ethyl acetoacetate is described. W. A. S.

Polymorphic Forms and Thermotropic Properties of Schiff's Bases derived from 5-Iodo-4-hydroxy-3-methoxybenzaldehyde. R. M. HANN (*J. Washington Acad. Sci.*, 1924, **14**, 79—86).—Derivatives of the Schiff base type have been prepared from 5-iodo-4-hydroxy-3-methoxybenzaldehyde and aromatic amines. These 5-iodovanillidene compounds are not phototropic, but on vigorous trituration they change colour owing to the production of polymorphic forms. The introduction of iodine into *p*-hydroxy-*m*-methoxybenzaldehyde results in the disappearance of the power to undergo thermotropic change in the vanillidene derivatives. The following compounds are described: 5-*iodovanillideneaniline*, deep red bipyramids, changing to an orange powder, m. p. 152—153°; 5-*iodovanillidene*-o-*chloroaniline*, yellowish-brown crystals, m. p. 143°; 5-*iodovanillidene*-p-*chloroaniline*, red needles, changing to an orange powder, m. p. 110—111° (decomp.); 5-*iodovanillidene*-p-*bromoaniline*, yellowish-brown powder, changing to yellowish-green, with metallic lustre, m. p. 108° (partial decomp.); 5-*iodovanillidene*-p-*iodoaniline*, yellowish-brown powder, changing to yellowish-green with metallic lustre, m. p. 98°; 5-*iodovanillidene*-o-*toluidine*, light yellow needles, changing to deep yellow, m. p. 120—121°; 5-*iodovanillidene*-m-*toluidine*, orange-red granules, darkening on trituration, m. p. 103—104°; 5-*iodovanillidene*-p-*toluidine*, brilliant golden-yellow crystals, becoming nearly colourless on trituration, m. p. 160—161°; 5-*iodovanillidene*-α-*naphthylamine*, yellowish-brown crystals, changing to bright yellow, decomposes at 226°; 5-*iodovanillidene*-β-*naphthyl*-

amine, light yellow needles, changing to deep yellow, m. p. 163°; *5-iodovanillidene-ψ-cumidine*, chocolate-brown powder, changing to yellow, m. p. 165°; *5-iodovanillidenebenzidine*,

$$C_6H_4I(OMe)(OH)\cdot CH{:}N\cdot C_6H_4\cdot C_6H_4\cdot NH_2,$$

bright orange flocks, crimson on trituration, m. p. 160—161° (incipient decomp.). R. B.

o-Methoxydiphenylacetaldehyde and its Transformations. R. Stoermer and F. Frick (*Ber.*, 1924, **57**, [*B*], 23—29).—*αα-o-Methoxydiphenylethylene glycol*, $MeO\cdot C_6H_4\cdot CPh(OH)\cdot CH_2\cdot OH$, long needles, m. p. 96°, prepared in moderate yield by the action of magnesium *o*-anisyl bromide on benzoylcarbinol, is smoothly converted by hot sodium hydrogen sulphite solution into *o-methoxydiphenylacetaldehyde*, a viscous liquid, b. p. 198°/16 mm.; the corresponding *semicarbazone* has m. p. 175°, whereas an oxime or a phenylhydrazone could not be isolated. The aldehyde is converted by glacial acetic and hydrobromic acids into 1-phenylcoumarone, m. p. 120°, instead of the expected 2-phenyl derivative. Probably the migration of the phenyl group takes place in an intermediately formed tolane derivative which could not be isolated. The aldehyde is transformed by phosphorus pentachloride into *α-chloro-ββ-o-methoxydiphenylethylene*, b. p. 190°/11 mm., which, however, is converted by sodium ethoxide at 200° immediately into 1-phenylcoumarone.

o-Methoxydiphenylacetaldehyde is decomposed by an excess of alcoholic potassium hydroxide solution at 180—200° into potassium formate and *o-methoxydiphenylmethane*, long, colourless needles, m. p. 30°, the constitution of which is established by its formation from *o*-methoxybenzophenone by Clemmensen's method; the corresponding *phenylurethane* has m. p. 115°. The methoxy derivative is converted by glacial acetic and hydrobromic acids at 150° into *o-hydroxydiphenylmethane*, b. p. 175°/18 mm., m. p. 15°.

The aldehyde is oxidised in acetone solution by potassium permanganate in the presence of potassium carbonate to *o-methoxydiphenylacetic acid*, m. p. 125°; it is reduced by aluminium amalgam in the presence of moist ether to *o-methoxydiphenylethyl alcohol*, a colourless, very viscous liquid, b. p. 220°/30 mm. (*phenylurethane*, m. p. 107°; *benzoate*, m. p. 98°), which is converted by acetic and hydrobromic acids into 2-phenylcoumaran, m. p. 39°, together with much resinous matter.

as-*o-Methoxydiphenylethylene oxide*, m. p. 90°, is obtained as a by-product of the preparation of *αα-o*-methoxydiphenylethylene glycol; it is transformed by dilute hydrochloric acid at 180° into methoxydiphenylacetaldehyde. H. W.

Action of Piperidine on Phenyl α-Bromostyryl Ketone. Production of a New Ketone, Phenylbenzylglyoxal. C. Dufraisse and H. Moureu (*Compt. rend.*, 1924, **178**, 573—575; cf. A., 1922, i, 843; 1923, i, 113).—Piperidine converts phenyl α-bromostyryl ketone into *phenyl α-bromo-β-phenyl-α-piperidinoethyl ketone*, $COPh\cdot CBr(NC_5H_{10})\cdot CH_2Ph$, a pale yellow, sparingly

soluble substance, m. p. 164°, very unstable, but forming stable salts with acids. This ketone, with 1 mol. of alkali in alcoholic solution, affords the red piperidinobenzylideneacetophenone described by Watson (T., 1904, **85**, 1322) and now shown to be phenyl α-piperidinostyryl ketone, $COPh{\cdot}C(NC_5H_{10}){:}CHPh$. The latter substance, on hydrolysis by acid, is converted into *phenylbenzylglyoxal*, $Bz{\cdot}CO{\cdot}CH_2Ph$, a pale yellow solid, m. p. 67—68°, unstable in air, but stable in a vacuum. E. E. T.

Additive Compounds of Metallic Salts and Doubly Unsaturated Aromatic Ketones. W. Dilthey and O. Rauchhaupt (*Ber.*, 1924, **57**, [*B*], 309—310).—Concentrated solutions of di-*p*-methoxystyryl ketone and ferric chloride in glacial acetic acid yield the additive *compound*, $[(OMe{\cdot}C_6H_4{\cdot}CH{:}CH)_2CO]_2,FeCl_3$, dark violet needles, m. p. 146° after previous decomposition. In a similar manner, o-*chlorostyryl methoxystyryl ketone*, yellow crystals, m. p. 109°, gives the *compound*, $C_{36}H_{30}O_2Cl_4Fe$, dark violet needles, m. p. 155—156° (decomp.). Uranyl chloride and distyryl ketone yield the product, $[(CHPh{:}CH)_2CO]_2,UO_2Cl_2$, small, golden-yellow leaflets, m. p. 264° after incipient decomposition at 200°; the corresponding *compound*, $C_{38}H_{36}O_8Cl_2U$, from di-*p*-methoxystyryl ketone, crystallises in violet-red, hexagonal leaflets, m. p. about 258° (incipient decomp. 150°). The additive *compound*, $[(C_6H_4[OMe]{\cdot}CH{:}CH)_2CO]_2,VCl_2$, brownish-yellow needles, is prepared from its components dissolved in glacial acetic acid. H. W.

Synthesis of Nitranilic Acid. H. O. Meyer (*Ber.*, 1924, **57**, [*B*], 326—328).—Nitranilic acid [3 : 6-dinitro-2 : 5-dihydroxy-*p*-benzoquinone] is obtained in 72—78% yield by the action of fuming nitric acid (*d* 1·459) on *p*-benzoquinone at −5° to −10°. It crystallises in lemon-yellow needles, m. p. 86—87°, whereas Nietzki (A., 1911, i, 69) gives m. p. 100°. The potassium salt, $C_6O_8N_2K_2$, exists in two distinct crystalline forms. The *rubidium* salt, $C_6O_8N_2Rb_2$, yellow needles, is described. H. W.

Action of Potassium Ferricyanide on Purpurin in Alkaline Solution. R. Scholl and P. Dahll (*Ber.*, 1924, **57**, [*B*], 80—83).—Purpurin is readily oxidised in alkaline solution by potassium ferricyanide at the atmospheric temperature to *o*-phthalic acid and 2 : 5-dihydroxy-*p*-benzoquinone, *o*-2 : 5-dihydroxy-*p*-benzoquinonoylbenzoic acid being apparently produced initially. The first stage of the oxidation of purpurin is therefore similar to that of alizarin (Scholl and Zinke, A., 1919, i, 25; 1920, i, 169) and quinizarin (this vol., i, 178). Dihydroxyanthraquinones which contain the hydroxy group attached to different nuclei and monohydroxyanthraquinones are not affected by potassium ferricyanide in alkaline solution at the atmospheric temperature. The hypothesis that oxidative fission occurs through the diquinones therefore receives further support.

In addition to the orange-yellow modification described in the

literature, 2 : 5-dihydroxy-*p*-benzoquinone exists in a pale yellow, metastable *modification* which is stable only in the presence of acetic acid. The substance is readily converted by methyl-alcoholic hydrogen chloride into the dimethyl ether. H. W.

Dyestuffs of the Phenanthrene Series. K. Brass (*Z. angew. Chem.*, 1924, **37**, 67—69).—Phenanthraquinonyl azides behave in a similar manner to phenyl azides towards sulphuric acid. Thus, 2-azidophenanthraquinone yields 2-amino-3-hydroxyphenanthraquinone, from which 2 : 3-dihydroxyphenanthraquinone is prepared in the usual manner, some 2-aminophenanthraquinone being formed at the same time. Under certain conditions 4-azidophenanthraquinone yields, with sulphuric acid, 4-amino-1-hydroxyphenanthraquinone, and under others 1 : 4-dihydroxyphenanthraquinone. These compounds are dyestuffs for wool and cotton. The presence of a hydroxyl group in the *o*-position to an amino- or a hydroxyl group has little or no effect on the tinctorial properties of the parent compounds, whereas its presence in the *p*-position to such groups greatly enhances their value. As mordant dyestuffs the 4-amino-1-hydroxy and 1 : 4-dihydroxy compounds are more powerful than the 2-amino-3-hydroxy and 2 : 3-dihydroxy compounds. The simple aminophenanthraquinones are also dyestuffs for wool, and possess more powerful tinctorial properties than the simple aminoanthraquinones. [Cf. *B.*, 1924, 246.] W. T. K. B.

Azido-, Aminohydroxy-, and Dihydroxy-phenanthraquinones. I. K. Brass, E. Ferber, and J. Stadler (*Ber.*, 1924, **57**, [*B*], 121—128).—2-Aminophenanthraquinone behaves as an amine of the benzene series, in which the basic character is repressed by the presence of acidic groups; its diazotisation and the conversion of its diazonium hydrogen sulphate into a series of derivatives are described.

2-Aminophenanthraquinone is conveniently diazotised in accordance with the method of Schmidt and Soll (A., 1908, i, 996), somewhat less advantageously in the presence of concentrated sulphuric acid. *Phenanthraquinone-2-diazonium perbromide*, $C_{14}H_7O_2N_2Br_3$, orange-yellow crystals which lose bromine at the atmospheric temperature, is prepared by treating a solution of the diazonium sulphate with an excess of bromine dissolved in potassium bromide solution. It is transformed by ice-cold ammonia solution (25%) into *2-azidophenanthraquinone*, cinnabar-red leaflets, m. p. 186° (decomp.) after darkening at 175°, which is converted by *o*-phenylenediamine hydrochloride into *2-azidophenanthraphenazine*, $C_{20}H_{11}N_5$, long, yellow needles, m. p. 190° (decomp.) after softening at 180°. The action of sulphuric acid on the azide gives a mixture of 2-aminophenanthraquinone and *2-amino-3-hydroxyphenanthraquinone*, bluish-black needles, which softens at 120°, but does not melt in a capillary tube at a higher temperature. The mixture of products yields phthalic acid when oxidised. 2 : 3-*Dihydroxyphenanthraquinone*, prepared by diazotisation of the hydroxy-

amine in concentrated sulphuric acid solution, crystallises in slender, reddish-brown needles which have no definite melting point; it yields a *mono-sodium* salt and a *quinoxaline* derivative, small, orange-yellow needles, m. p. 162° (decomp.). H. W.

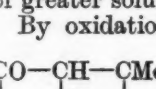
Azido-, Aminohydroxy-, and Dihydroxy-phenanthraquinones. II. K. Brass and J. Stadler (*Ber.*, 1924, **57**, [*B*], 128—136).—4-Aminophenanthraquinone is converted by sodium nitrite in the presence of concentrated sulphuric acid into the corresponding diazonium salt, which is relatively unstable in comparison with phenanthraquinone-2-diazonium sulphate (preceding abstract). It is transformed by a solution of bromine in concentrated potassium bromide solution into *phenanthraquinone-4-diazonium perbromide*, an orange-red, crystalline powder, from which 4-*azidophenanthraquinone*, red needles, is obtained by the action of aqueous ammonia (10%). 4-*Azidophenanthraphenazine*, prepared from the azide and *o*-phenylenediamine hydrochloride, crystallises in slender, yellow needles, m. p. 197° (decomp.). 4-Azidophenanthraquinone reacts with dilute sulphuric acid with unexpected ease, and after prolonged treatment at the temperature of boiling water yields solely 1 : 4-*dihydroxyphenanthraquinone*, very slender, bluish-violet needles (1 : 4-*diacetoxyphenanthraquinone*, prisms, m. p. 183°; 1 : 4-*dihydroxyphenanthraphenazine*, brownish-red, lustrous needles, m. p. 288°). The attachment of the two hydroxy groups to the same benzene nucleus is established by the observation that phthalic acid is the only isolable product of its oxidation. The compound must therefore be either 1 : 4- or 3 : 4-dihydroxyphenanthraquinone, and, since the latter constitution has already been assigned to morpholquinone, from which the present compound is quite distinct, the former alternative is selected. It appears, however, to be quite exceptional for a substituent to enter the phenanthraquinone nucleus in the 1-position. Oxidation of 1 : 4-dihydroxyphenanthraquinone in ethereal solution with silver oxide or lead tetra-acetate leads to the formation of a yellow *op-diquinone* which has not been isolated in the homogeneous condition.

4-*Amino*-1-*hydroxyphenanthraquinone* is prepared by the action of sulphuric acid on the azide at a temperature not exceeding 90°. It crystallises in violet-black aggregates of needles, decomp. 218° after subliming at 165°. The *sulphate* and the *hydrochloride* are described; the *sodium* salt is hydrolysed by water. It is transformed by hot, dilute sulphuric acid into 1 : 4-dihydroxyphenanthraquinone. H. W.

Formation of Diketocamphane (Ketocamphor) and of Diketofenchane (Ketofenchone) by the Oxidation of Camphor and Fenchone with Chromic Acid. J. Bredt (*J. pr. Chem.*, 1923, **106**, 336—347).—The *p*-diketocamphane described by Bredt and Goeb (A., 1921, i, 257) has now been obtained by the oxidation of both natural and inactive synthetic camphor with chromic acid. The product in both cases melts at 210° and the yield is only 4—5% of the theoretical. In its physiological action, *p*-di-

ketocamphane is similar to camphor, and it has the advantage of greater solubility in water.

By oxidation of fenchone in glacial acetic acid solution with chromic acid below 15° (the reaction takes about 5 weeks), *ketofenchone* is obtained, probably having the annexed formula. It forms long, thin needles, m. p. 42·5—43°, has a typical lactone odour, and is readily volatile in steam; b. p. 108°/10·5 mm. The new keto group is more active than the original keto group of fenchone, and there are readily formed a *monophenylhydrazone*, white needles, m. p. 149—150° (decomp.), and a *monosemicarbazone*, thin needles, m. p. 222—223°. Ketofenchone has $[\alpha]_D^{21}$ +75·78° in benzene. E. H. R.



Solubility of Sulphur in Caoutchouc. W. J. Kelly and K. B. Ayers (*Ind. Eng. Chem.*, 1924, **16**, 148—150).—The distribution of dissolved sulphur between unvulcanised rubber and amyl or *n*-butyl alcohol obeys Henry's law. The sulphur consequently is present in the rubber in a state of solution and not of adsorption. For the determination of the solubility of sulphur in rubber it is convenient to suspend strips of the latter in a saturated solution of sulphur in butyl alcohol in the presence of solid sulphur; when equilibrium is attained, the dissolved sulphur is extracted from the rubber with acetone and its amount determined. [Cf. *B.*, 1924, 266.] D. F. T.

Reduction Products of 1-Acylcoumarones. R. Stoermer, C. W. Chydenius, and E. Schinn (*Ber.*, 1924, **57**, [*B*], 72—80).—1-Acetylcoumarone, b. p. 136°/11 mm., m. p. 76° (cf. Stoermer and Schäffer, A., 1903, i, 846), is prepared conveniently by the action of chloroacetone on salicylaldehyde and potassium hydroxide dissolved in alcohol; the *phenylhydrazone*, pale yellow crystals, m. p. 153—154°, and the *semicarbazone*, colourless needles, m. p. 217°, are described. Reduction of the ketone by sodium amalgam in the presence of alcohol acidified with acetic acid yields coumaranylmethylcarbinol, $C_6H_4<^{O}_{CH_2}>CH\cdot CHMe\cdot OH$, and *acetylcoumarane*, $C_6H_4<^{O}_{CH_2}>CHAc$, a colourless liquid, b. p. 132—133°/12 mm. (the sodium hydrogen sulphite *compound*, the *oxime*, m. p. 111—112°, the *phenylhydrazone*, yellow leaflets, m. p. 113°, and the *semicarbazone*, m. p. 192°, are described). *Diacetylbiscoumarane*, $C_{20}H_{18}O_4$, m. p. 183°, gives a *mono-oxime*, m. p. 177°. Reduction of acetylcoumaraneoxime by sodium amalgam and alcohol leads to the formation of small quantities of 1-*α-aminoethylcoumarane*, $C_6H_4<^{O}_{CH_2}>CH\cdot CHMe\cdot NH_2$, a fairly mobile liquid, b. p. 153°/15 mm. (*hydrochloride*, colourless, lustrous leaflets, m. p. 117—118°; *picrate*, yellow leaflets, decomp. 209°).

Reduction of acetylcoumarone with sodium and alcohol according to the method of Stoermer and Schäffer (*loc. cit.*) gives acetylcoumarane, coumaranylmethylcarbinol, and *o*-hydroxyphenyl-

butan-γ-ol, m. p. 66—67°; the latter substance may also be obtained by reduction of coumaranylmethylcarbinol. It is converted by bromine in chloroform solution into *4-bromo-2-hydroxyphenylbutan-γ-ol*, long, colourless needles, m. p. 94—95°. *o-Methoxyphenylbutan-γ-ol*, a colourless, viscous liquid, b. p. 143°/12 mm., is prepared by the action of methyl iodide and potassium hydroxide on an alcoholic solution of the corresponding phenol. It is converted by zinc chloride at 150° into *o*-Δ^{β}-butenylanisole, b. p. 104—106°/12 mm., d_4^{19} 0·9721, n_D^{19} 1·5255 (cf. von Braun and Schirmacher, A., 1923, i, 286), which is isomerised when heated with a small quantity of potash-lime to o-Δ^{α}-*butenylanisole*, b. p. 106—108°/12 mm., d_4^{18} 0·9819, n_D^{18} 1·5346.

1-iso*Propenylcoumarane*, $C_6H_4<\begin{matrix}O\\CH_2\end{matrix}>CH\cdot CMe{:}CH_2$, a mobile liquid, b. p. 106—108°/12 mm., is obtained together with much resinous matter by the action of magnesium methyl iodide on acetylcoumarane.

1-Benzoylcoumarone, m. p. 90—91° (*semicarbazone*, m. p. 137°), is conveniently obtained by the action of bromoacetophenone and potassium hydroxide on salicylaldehyde in alcoholic solution. Somewhat unexpectedly, it is reduced by sodium and alcohol mainly to 1-*benzylcoumarane*, m. p. 26°, b. p. 185°/15 mm.; small quantities of β-o-*hydroxyphenylethylphenylcarbinol*,

$$OH\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot CHPh\cdot OH,$$

slender needles, m. p. 94° (*phenylurethane*, m. p. 124°; *diphenylurethane*, m. p. 52°), are simultaneously produced. *Coumaronylphenylcarbinol*, $C_6H_4<\begin{matrix}O\\CH\end{matrix}>C\cdot CHPh\cdot OH$, m. p. 76°, is obtained by the reduction of benzoylcoumarone with sodium amalgam in acid-alcoholic solution at the atmospheric temperature; the corresponding *phenylurethane* has m. p. 126°. *Benzoylcoumarone-oxime*, m. p. 132°, is reduced by sodium amalgam in faintly acid, alcoholic solution to *coumaronylphenylaminomethane*, a colourless liquid, b. p. 200°/11 mm. (*hydrochloride*, m. p. 210°). It is converted by one molecular proportion of sodium nitrite into coumarylphenylcarbinol and by two molecular proportions into benzoylcoumarone; it is reduced by sodium and alcohol to benzoylcoumarane. 1-*Benzylcoumarone*, b. p. 180—185°/15 mm., cannot be prepared from the benzoyl compound by Clemmensen's method, but is obtained when the hydrazone is heated with an alcoholic solution of sodium ethoxide at 220—230°. Attempts to prepare it by converting coumarylphenylcarbinol by means of thionyl chloride into coumarylphenylmethyl chloride and reduction of the latter substance with zinc dust and acetic acid yielded a *compound*, $C_{30}H_{26}O_2$, m. p. 98°, probably 1 : 1′-dibenzyl-2 : 2′-dicoumarane. H. W.

Synthesis of 4-Ketochroman [Chromanone]. F. MAYER and L. VAN ZÜTPHEN (*Ber.*, 1924, **57**, [*B*], 200—202; cf. Arndt and Källner; Krollpfeiffer and Schultze, succeeding abstracts).—β-Chloropropionyl chloride is converted by phenol in the presence of carbon disulphide and aluminium chloride or phosphoryl chloride

into a mixture of phenyl β-chloropropionate, b. p. 132—135°/12 mm., and a *substance*, $C_9H_{10}O_3$, m. p. 141—142°, which is regarded provisionally as *o*(?*p*)-hydroxyphenyl β-hydroxyethyl ketone. The ester is transformed by aluminium chloride into o-*hydroxyphenyl β-chloroethyl ketone*, colourless prisms, m. p. 70°, and p-*hydroxyphenyl β-chloroethyl ketone*, colourless, lustrous leaflets, m. p. 90° (m. p. 75—80°, directly after crystallisation from water), which are separated from one another by distillation with steam, with which only the ortho-derivative is volatile; the compound $C_9H_{10}O_3$ (above) is also formed in small amount. The ortho-compound is converted by aluminium chloride at 160—180° into 4-*ketochroman* [*chromanone*], $C_6H_4<\begin{matrix}CO\cdot CH_2\\ O-CH_2\end{matrix}$, colourless, slender needles, m. p. 111°, b. p. 128°/13 mm. (the *sodium* salt, yellow crystals, the *oxime*, long, colourless needles, m. p. 144—145°, and the *benzylidene* derivative, m. p. 147—150°, are described). H. W.

Chromanone and Chromonol. F. Arndt and G. Källner (*Ber.*, 1924, **57**, [*B*], 202—206; cf. Mayer and van Zütphen, preceding abstract; Krollpfeiffer and Schultze, succeeding abstract).—β-Phenoxypropionic acid is converted by concentrated sulphuric acid or, more advantageously from the point of view of yield, by successive treatment with phosphorus pentachloride and aluminium chloride in the presence of benzene, into *chromanone*, colourless plates, b. p. 127—128°/13 mm., m. p. 38° (Mayer and van Zütphen, *loc. cit.*, give m. p. 111°); 3-*benzylidenechromanone*, almost colourless crystals, has m. p. 113° (Mayer and van Zütphen give m. p. 147—150°). Chromanone condenses with *p*-nitrosodimethylaniline in alcoholic solution in the presence of potassium hydroxide and the product is reduced by hydrazobenzene to (?)3-p-*dimethylaminophenylaminochromanone*, $C_6H_4<\begin{matrix}CO\cdot CH\cdot NH\cdot C_6H_4\cdot NMe_2\\ O-CH_2\end{matrix}$, golden-yellow leaflets, m. p. 154° (the colourless *hydrochloride* is described), which is oxidised by potassium ferricyanide to the corresponding, very unstable anil. The latter substance is converted by boiling, concentrated hydrochloric acid into *chromonol* (3-*hydroxy*-1 : 4-*benzopyrone*), $C_6H_4<\begin{matrix}CO\cdot C(OH)\\ O-CH\end{matrix}$, coarse, colourless needles, m. p. 181°; the *sodium*, *calcium*, and *magnesium* derivatives are described. The *benzoate* crystallises in colourless needles, m. p. 177·5°. 3-*Bromochromanone* has m. p. 69—70°. H. W.

Ring Closures from β-Phenoxypropionic Acids to Chromanones. F. Krollpfeiffer and H. Schultze (*Ber.*, 1924, **57**, [*B*], 206—207; cf. Mayer and van Zütphen; Arndt and Källner, preceding abstracts).—The formation of chromanones from β-phenoxyphenylpropionic acids is most conveniently effected by heating mixtures of the latter and phosphoric anhydride under diminished pressure; the action of concentrated sulphuric acid or of phosphoric oxide in the presence of benzene is less suitable. *Chromanone* crystallises in colourless leaflets, m. p. 39—40°, b. p.

124°/14 mm.; the *semicarbazone*, small, colourless needles, has m. p. 227°. β-p-*Toloxypropionic acid*, colourless needles, m. p. 147—148°, yields 6-methylchromanone, m. p. 34—36° (cf. von Auwers and Krollpfeiffer, A., 1915, i, 442). H. W.

Syntheses of Chromones and Coumarins. G. Wittig (*Ber.*, 1924, **57**, [*B*], 88—95).—Chromones are readily obtained by condensation of *o*-acetylphenols with sodium and ethyl acetate, followed by ring closure of the diketones thus produced.

The displacement of the acetyl group into the ortho position to the hydroxy radical is effected by heating the phenolic esters with aluminium chloride at 110—115°; 4-chloro-6-acetylphenol (3-chloro-6-hydroxyphenyl methyl ketone), m. p. 53·5—54·7°, 4-*chloro*-6-*acetyl*-m-*cresol*, colourless needles, m. p. 69—70°, and 6-acetyl-*p*-cresol, m. p. 45—46°, are described.

4-Chloro-6-acetylphenol is converted by acetic anhydride and sodium acetate at 160—170° into a mixture of 6-chloro-4-methylcoumarin, m. p. 186—187°, and 6-*chloro*-2-*methylchromone*, $C_6H_3Cl<\begin{matrix}CO\cdot CH\\ \|\\ O-CMe\end{matrix}$, colourless needles, m. p. 115—116°. The substances are separated from one another by means of an alcoholic solution of sodium ethoxide, which causes fission of both rings with the production of 5-*chloro*-β-*methylcoumaric acid*, m. p. 156° (decomp.), and 4-chloro-6-acetylacetophenol. Addition of acid converts the former into its lactone, whereas the latter can be removed by aqueous sodium hydroxide and subsequently reconverted into its cyclic compound by sulphuric acid. The mixture of chromone and coumarone is converted by boiling 2*N*-sodium hydroxide solution into 5-chlorosalicylic acid, m. p. 173—174°, which owes its formation to fission of the intermediately formed diketone, $OH\cdot C_6H_3Cl\cdot CO\cdot CH_2\cdot COMe$.

A similar series of reactions has been applied to 4-chloro-6-acetyl-*m*-cresol, whereby the following compounds are produced: 6-*chloro*-4 : 7-*dimethylcoumarin*, needles, m. p. 206—207°; 4-*chloro*-6-*acetyl*-*aceto*-m-*cresol*, pale yellow, lustrous leaflets, m. p. 115·5—116·5°; 6-*chloro*-2 : 7-*dimethylchromone*, needles, m. p. 144·5—145·5°; 5-chloro-4-methylsalicylic acid, m. p. 203—204°. Similarly, 6-acetyl-*p*-cresol gives 2 : 6-dimethylchromone, m. p. 99·5—100°, 4 : 6-dimethylcoumarin, m. p. 147·5—148°, and 5-methylsalicylic acid, m. p. 148·5—149°.

p-Chlorophenyl methyl ether is converted by acetyl chloride and aluminium chloride in the presence of carbon disulphide into 4-*chloro*-6-*acetylphenyl methyl ether*, needles, m. p. 29—30°, which is transformed by sodium and ethyl acetate into 4-*chloro*-6-*acetylacetophenyl methyl ether*, yellow prisms, m. p. 76·5—77·5°; the latter compound is converted by concentrated hydriodic acid or, less advantageously, by hydrobromic and glacial acetic acids into 6-chloro-2-methylchromone.

The preparation of 6-chloro-2-methylchromone, 6-chloro-2 : 7-dimethylchromone, and 2 : 6-dimethylchromone by the action of sodium and ethyl acetate on the requisite phenol is described.

4-*Chloro*-6-*acetylacetophenol* crystallises in pale yellow leaflets, m. p. 110—111°; 6-*acetylaceto*-p-*cresol* has m. p. 94·5—96°.

H. W.

Interaction of Ethyl Acetoacetate with *o*-Hydroxystyryl Ketones. T. A. FORSTER and I. M. HEILBRON (*J. Chem. Soc.*, 1924, **125**, 340—347).—2-Hydroxystyryl methyl ketone condenses with ethyl acetoacetate, in presence of sodium ethoxide or aqueous sodium hydroxide, to give 4-*acetonyl*-2-*methyl*-γ-*pyran*,

$$C_6H_4<\begin{matrix}CH(CH_2Ac)\cdot CH\\ O\text{———}CMe\end{matrix}>,$$

colourless needles, m. p. 134—135° (*phenylhydrazone*, colourless needles, m. p. 200°). Condensation of 2-hydroxystyryl phenyl ketone with ethyl benzoylacetate similarly affords 2-*phenyl*-4-*phenacyl*-γ-*pyran*, colourless crystals, m. p. 130°, together with 2-*phenyl*-4-*phenacyl*-γ-*pyran*-3-*carboxylic acid*, colourless prisms, m. p. 157°. Condensation of 2-methoxystyryl methyl ketone with ethyl acetoacetate affords *ethyl* 3-o-*methoxyphenyl*-5-*methyl*-Δ^5-cyclo*hexen*-1-*one*-2(or 4)-*carboxylate*, $\begin{matrix}CH_2\text{———}CMe{:}CH\\ OMe\cdot C_6H_4\cdot CH\cdot CH(CO_2Et)\cdot CO\end{matrix}$ or $\begin{matrix}CH(CO_2Et)\cdot CMe{:}CH\\ OMe\cdot C_6H_4\cdot CH\text{——}CH_2\text{——}CO\end{matrix}$, pale yellow needles, m. p. 139°.

2-*Methoxystyryl phenyl ketone* (colourless needles, m. p. 60°) condenses with ethyl acetoacetate to give *ethyl* 5-*phenyl*-3-o-*methoxyphenyl*-Δ^5-cyclo*hexen*-1-*one*-2-*carboxylate*, colourless prisms, m. p. 95°, whilst 2-hydroxystyryl phenyl ketone under similar conditions affords 3-*acetyl*-4-*phenacyldihydrocoumarin*,

$$C_6H_4<\begin{matrix}CH(CH_2Bz)\cdot CHAc\\ O\text{———}CO\end{matrix}>,$$

colourless needles, m. p. 175°, together with a small quantity of a colourless crystalline *substance*, m. p. 214°.

6-, 7-, and 8-*Methoxy*-4-*acetonyl*-2-*methyl*-γ-*pyran* respectively form feathery needles, m. p. 119°, colourless crystals, m. p. 149°, and colourless needles, m. p. 168°, the 8-compound affording a colourless, crystalline *phenylhydrazone*, m. p. 186°.

Spectrographic measurements support certain of the above constitutional formulæ.

F. G. W.

The Brazilin and Hæmatoxylin Question. III. The Degradation Product of Brazilin obtained by Schall and Dralle. P. PFEIFFER and J. OBERLIN (*Ber.*, 1924, **57**, [*B*], 208—213; cf. A., 1917, i, 661; 1920, i, 561).—The compound, $C_9H_6O_4$, isolated by Schall and Dralle (A., 1892, 502) by the action of atmospheric oxygen on an alkaline solution of brazilin has been considered by Feuerstein and von Kostanecki (A., 1899, i, 538) to be 3 : 7-dihydroxychromone, $HO\cdot C_6H_3<\begin{matrix}O\text{—}CH\\ CO\cdot C\cdot OH\end{matrix}>$. This is confirmed by the observation that synthetic 3 : 7-dimethoxychromone is identical with the dimethyl ether of the degradation product.

β-3-*Methoxyphenoxypropionic acid*, $OMe\cdot C_6H_4\cdot O\cdot CH_2\cdot CH_2\cdot CO_2H$,

colourless, lustrous crystals, m. p. 81—83°, is prepared in poor yield (17%) from resorcinol methyl ether and β-iodopropionic acid. It is converted by treatment with zinc chloride at 145°, with phosphoric anhydride at about 100°, or by the successive action of phosphorus pentachloride and aluminium chloride, into 7-methoxychromanone, identical with the product obtained by Pfeiffer and Grimmer by the reduction of 7-methoxychromone (cf. A., 1917, i, 661). The chromanone is transformed by amyl nitrite and potassium amoxide in amyl alcoholic solution into *3-oximino-7-methoxychromanone* (*3-oximino-7-methoxy-2 : 3-dihydro-1 : 4-benzopyrone*), almost colourless, microscopic leaflets, m. p. 146—147° (decomp.), which, when treated with glacial acetic and dilute sulphuric acids, gives *3-hydroxy-7-methoxychromone* (*3-hydroxy-7-methoxy-1 : 4-benzopyrone*), colourless, microscopic needles, m. p. 171—172°. *3 : 7-Dimethoxychromone*, prepared from the preceding compound and methyl sulphate, forms colourless crystals, m. p. 169—170°. H. W.

Linear and Angular Diphthaloylthianthrens. K. Brass and K. Heide (*Ber.*, 1924, **57**, [*B*], 104—121).—An extension of the work on compounds containing the dithiin ring to anthracene derivatives. In these, the stability of the ring is much greater than in the corresponding naphthalene compounds (cf. Brass and Köhler, A., 1922, i, 1050), and its conversion by loss of an atom of sulphur into the thiophen ring is effected only under drastic conditions. Contrary to the views of Scholl and Seer (A., 1911, i, 557), both linear and angular diphthaloylthianthrens are well-defined vat dyes.

2 : 3 : 6 : 7-Diphthaloylthianthren,

$$C_6H_4\langle\begin{matrix}CO\\CO\end{matrix}\rangle C_6H_2\langle\begin{matrix}S\\S\end{matrix}\rangle C_6H_2\langle\begin{matrix}CO\\CO\end{matrix}\rangle C_6H_4$$

(cf. Scholl and Seer, *loc. cit.*), is prepared by heating a mixture of molecular proportions of 2 : 3-dibromoanthraquinone and crystalline sodium sulphide gradually to 210° under pressure; it crystallises in small, brown needles which do not melt below 360°. It is remarkably stable towards nitric acid. It is reduced by alkaline sodium hyposulphite or by zinc dust and alkali hydroxide to *tetrahydroxydinaphthathianthren*, pale greenish-yellow needles; the *tetrabenzoate*, golden-yellow needles, which darken at 320° but do not melt below 350°, is hydrolysed and oxidised by concentrated sulphuric acid to benzoic acid and diphthaloylthianthren.

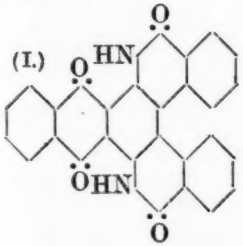
2 : 3-Dibromoquinizarin is transformed by boiling acetic anhydride in the presence of fused zinc chloride into the corresponding *diacetate*, pale yellow needles, m. p. 242° (indefinite), and by benzoyl chloride in the presence of nitrobenzene into the *dibenzoate*, yellow needles. It is converted by an equimolecular proportion of crystalline sodium sulphide at a temperature not exceeding 190° into *1 : 4 : 5 : 8-tetrahydroxy-2 : 3 : 6 : 7-diphthaloylthianthren*, dark green needles with a metallic lustre which do not melt below 360°; the dithiin is more advantageously prepared by the action of sodium sulphide on an aqueous suspension of 2 : 3-dibromo-1 : 4 : 9 : 10-anthra-

diquinone (cf. Dimroth, Friedmann, and Kämmerer, A., 1920, i, 444) in the absence of air. When heated with nitric acid (*d* 1·52) on the steam-bath it loses almost exactly a molecular proportion of sulphur and is doubtless transformed into diquinizarinthiophen, which, however, has not been more closely investigated. The dithiin yields a *monosodium* salt, $C_{28}H_{11}O_8S_2Na$, a *di-sodium* salt, and a *di-potassium* salt; greater proportions of base could not be introduced into the molecule. It is converted by alkaline hyposulphite solution or by zinc dust and alkali hydroxide into a blood-red vat from which *octahydroxydianthracenedithiin* separates in brown flocks after addition of acid; it has m. p. 238—244°. The corresponding *octabenzoate* crystallises in pale yellow needles, m. p. 240—244°. Tetrahydroxydiphthaloylthianthren is converted by benzoyl chloride in the presence of boiling nitrobenzene into the corresponding *tetrabenzoate*, a greenish-yellow, crystalline powder which does not melt below 360°, and by acetic anhydride in the presence of dehydrating agents into the *diacetate*, brown leaflets.

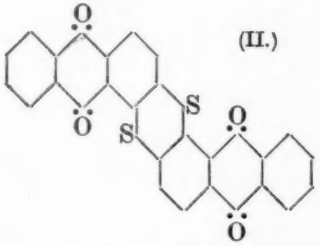
2 : 3-Dichloro-1 : 4-diaminoanthraquinone is converted by crystalline sodium sulphide at 210° into 1 : 4 : 5 : 8-*tetra-amino*-2 : 3 : 6 : 7-*diphthaloylthianthren*, $C_{28}H_{16}O_4N_4S_2$, small, dark blue needles which do not melt below 360°; with alkaline sodium hyposulphite solution it yields a red vat from which ammonia is evolved at 50—60°. Benzoylation of the vat leads to the production of the expected *octabenzoyl* derivative, $C_{84}H_{52}O_{12}S_2$, long, pale yellow, prismatic needles, m. p. 302° (decomp.). 1 : 4 : 5 : 8-*Tetrabenzoylamino*-2 : 3 : 6 : 7-*diphthaloylthianthren* crystallises in small, greenish-yellow, lustrous needles, which do not melt below 360°.

The presence of two benzoylamino groups in the vicinal position to the halogen atoms of 2 : 3-dichloro-1 : 4-dibenzoylaminoanthraquinone appears to inhibit the formation of the dithiin ring, since the substance is converted by sodium sulphide at 180° into the phenanthridone (I), microscopic, green needles which do not melt below 300°.

(I.)



(II.)



3 : 4 : 7 : 8-*Diphthaloylthianthren* [*thioindanthren*] (II), dark green, coppery needles, which do not melt below 360°, is prepared from 1 : 2-dibromoanthraquinone and sodium sulphide at 190°. With alkaline sodium hyposulphite solution, it gives a blood-red vat from which the expected *tetrabenzoate*, yellow needles, is obtained by the action of benzoyl chloride. H. W.

Hydroxypyrrole Derivatives [IV] and certain Reactions of Chloroacetyldiacetonitriles. E. BENARY and G. SCHWOCH (*Ber.*, 1924, **57**, [*B*], 332—339; cf. Benary and Lau, A., 1923, i, 366).—The remarkable formation of dyes when treated with alcoholic or liquid ammonia appears to be a general property of halogenoacyl derivatives of dinitriles containing an aromatic substituent and an unsubstituted imino group; when the latter contains a substituent, the normal formation of hydroxypyrroles is observed.

Chloroacetyldiacetonitrile, $NH_2 \cdot CMe{:}C(CN) \cdot CO \cdot CH_2Cl$, is converted by methyl-alcoholic ammonia into 4-*hydroxy*-2-*methylpyrrole*-3-*nitrile*, $HN<\begin{matrix}CMe{:}C \cdot CN \\ CH{=}C \cdot OH\end{matrix}$, which is too unstable to permit its isolation in the homogeneous condition; it is characterised by its conversion into 5-*benzeneazo*-4-*keto*-2-*methylpyrroline*-3-*nitrile*, orange needles, decomp. 240°, by benzenediazonium solution, and by formaldehyde into *methylenebis*-4-*keto*-2-*methylpyrroline*-3-*nitrile*, an orange precipitate, decomp. about 250°.

C-*Chloroacetyl*-p-*toluacetodinitrile*, $NH_2 \cdot C(C_6H_4Me){:}C(CN) \cdot CO \cdot CH_2Cl$, matted needles, m. p. 166—168°, is prepared from *p*-toluacetodinitrile and chloroacetyl chloride in the presence of pyridine; it is converted by methyl-alcoholic ammonia into the *dye*, $\begin{matrix}C(CN) & CO \\ \| & \\ C(C_6H_4Me) \cdot NH\end{matrix}>C{:}C<\begin{matrix}C(CN){:}C \cdot C_6H_4Me \\ CH_2 \quad NH\end{matrix}, H_2O$, a dark, violet-red powder, decomp. about 200°. The chloro compound is transformed by potassium hydrogen sulphide in alcoholic solution into the corresponding *sulphide*, $[NH_2 \cdot C(C_6H_4Me){:}C(CN) \cdot CO \cdot CH_2]_2S$, colourless prisms, decomp. 218·5—220°.

p-*Methoxybenzoacetodinitrile*, coarse, colourless prisms, m. p. 118°, is prepared by the action of sodium wire on anisonitrile and acetonitrile dissolved in hot benzene. It is converted by treatment in warm alcoholic solution with dilute hydrochloric acid into p-*methoxyphenyl cyanomethyl ketone*, $C_6H_4(OMe) \cdot CO \cdot CH_2 \cdot CN$, prisms, m. p. 130·5°; this ketone, with phenylhydrazine and glacial acetic acid in cold alcoholic solution, affords the *phenylhydrazone*, soft needles, m. p. 135—136°, which when heated above its m. p. or boiled with dilute acetic acid passes into 5-*imino*-1-*phenyl*-3-p-*methoxyphenylpyrazolone*, $PhN<\begin{matrix}N{=}{=}{=}C \cdot C_6H_4 \cdot OMe \\ C(:NH) \cdot CH_2\end{matrix}$, lustrous leaflets, m. p. 188°. The dinitrile is converted by hydroxylamine hydrochloride in boiling, aqueous-alcoholic solution into 5-*imino*-3-p-*methoxyphenylisooxazolone*, prisms, m. p. 136—137°. C-*Chloroacetyl*-p-*anisylacetodinitrile*, $C_{12}H_{11}O_2N_2Cl$, needles, m. p. 164°, is converted by methyl-alcoholic ammonia into the dark, violet-red *dye*, $C_{24}H_{18}O_3N_4$ (cf. formula above), decomp. 200° after darkening at 185°, and by potassium hydrogen sulphide into the *sulphide*, $[OMe \cdot C_6H_4 \cdot C(NH_2){:}C(CN) \cdot CO \cdot CH_2]_2S$, a crystalline powder, m. p. 196—197° (decomp.) after darkening and softening at 190°.

C-*Chloroacetyl*-N-p-*anisyldiacetonitrile*, $C_{13}H_{13}O_2N_2Cl$, lustrous needles, m. p. 80—81·5°, is converted by alcoholic potassium

hydroxide solution into *3-hydroxy-1-p-anisyl-5-methylpyrrole-4-nitrile*, matted needles, m. p. 190—192° (decomp.).

N-Phenyl-α-anilinoacetylbenzoacetodinitrile, prepared from chloroacetylbenzoacetodinitrile and aniline, decomposes at 258—260° when rapidly heated; with mercuric chloride and dilute hydrochloric acid it yields the additive *compound*, $C_{23}H_{19}ON_3,HCl,HgCl_2$, pale yellow needles, m. p. 172°. When boiled with an excess of glacial acetic acid the base yields *α-acetanilidoacetyl-β-anilino-β-phenylacrylamide*, $NHPh\cdot CPh{:}C(CO\cdot CH_2\cdot NAcPh)\cdot CO\cdot NH_2$, colourless prisms, decomp. 296—298°, which is also obtained from chloroacetylbenzoacetodinitrile, aniline, and glacial acetic acid at 115—120°.

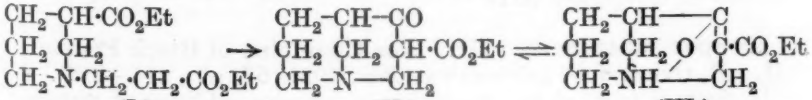
C-Anilinoacetyl-N-phenyldiacetonitrile,

$$NHPh\cdot CMe{:}C(CN)\cdot CO\cdot CH_2\cdot NHPh,$$

small needles, m. p. 214—216° when rapidly heated, is obtained from chloroacetyldiacetonitrile and aniline or from the latter and *C*-chloroacetyl-*N*-phenylbenzoacetodinitrile; it gives a lemon-yellow *picrate*, m. p. 165—166° after previous softening, and the additive *compound*, $C_{18}H_{17}ON_3,HCl,HgCl_2$, colourless needles, decomp. 230° after darkening at 215°.

The action of phenylhydrazine on chloroacetyldiacetonitrile leads somewhat unexpectedly to the production of *5-chloromethyl-1-phenyl-3-methylpyrazole-4-nitrile*, $PhN<\begin{matrix}N=\!=\!=CMe\\ |\quad\quad\quad|\\ C(CH_2Cl){:}C\cdot CN\end{matrix}$, needles, m. p. 130·5° after softening, which is also obtained from cyanoacetone phenylhydrazone and chloroacetyl chloride. It is hydrolysed to 5-hydroxymethyl-1-phenyl-3-methylpyrazole-4-carboxylic acid (cf. Benary, A., 1910, i, 434). Treatment with alcoholic potassium hydroxide solution transforms it into *5-ethoxymethyl-1-phenyl-3-methylpyrazole-4-nitrile*, slender needles, m. p. 68·5°, which is unaffected by boiling, concentrated hydrochloric acid. The chloride is converted by methyl-alcoholic ammonia at 50—60° into *5-aminomethyl-1-phenyl-3-methylpyrazole-4-nitrile*, long, colourless needles, m. p. 58—59° (*picrate*, pale yellow leaflets, m. p. about 250—251° [decomp.]) from which *5-hydroxymethyl-1-phenyl-3-methylpyrazole-4-nitrile*, needles, m. p. 114—116°, is obtained by means of nitrous acid. H. W.

Synthesis of a New Bicyclic Nitrogen Ring. *iso*Granatanine Derivatives. Preparation of an Isomeride of Homococaine. S. M. McElvain and R. Adams (*J. Amer. Chem. Soc.*, 1923, **45**, 2738—2750).—Ethyl nipecotinate (piperidine-3-carboxylate) on condensation with ethyl β-chloropropionate in alcoholic solution in the presence of silver oxide yields ethyl (3-carbethoxypiperidino)-propionate (I), this being converted by sodium in xylene solution into ethyl *iso*granatonine carboxylate (II).



Reduction of the ketone converts it into ethyl granatolinecarboxylate, and benzoylation of the latter yields a compound isomeric with homococaine. It is a less efficient local anæsthetic than cocaine, and is considerably more toxic than the latter.

Nicotinic acid nitrate was obtained by adding nicotine to nitric acid (*d* 1·42) and heating at 100° for several hours. The nitrate was converted into the hydrochloride by heating with hydrochloric acid, removing excess of the latter in a vacuum, dissolving the product in water, and precipitating with alcohol. Pure nicotinic acid was then obtained in the usual manner. Ethyl nicotinate was obtained by treating nicotinic acid (or its hydrochloride) successively with thionyl chloride and alcohol (excess of chloride being removed intermediately). Nipecotinic acid was prepared by the reduction of nicotinic acid hydrochloride with hydrogen in the presence of platinum oxide catalyst (cf. Freudenberg, A., 1919, i, 93). *Ethyl nipecotinate* is a colourless, water-soluble liquid, b. p. 102—104°/7 mm., d_{20}^{20} 1·0121, n_D^{19} 1·4592 (*hydrochloride*, needles, m. p. 110—111°); it may also be obtained (less satisfactorily) by the catalytic reduction of ethyl nicotinate hydrochloride in alcoholic solution, and by the reduction of ethyl nicotinate in alcoholic acetic acid. *Ethyl* (3-*carbethoxypiperidino*)*acetate*, obtained from ethyl nipecotinate and ethyl chloroacetate in presence of finely powdered silver oxide, has b. p. 147—149°/5 mm., d_{20}^{20} 1·0684, n_D^{18} 1·4607. The free *acid*, obtained by hydrolysis of the ester or by condensing nipecotinic acid with chloroacetic acid in the presence of hydrochloric acid, forms white crystals, m. p. 268—270° (decomp.). *Ethyl* (3-*carbethoxypiperidino*)*propionate*, obtained similarly from ethyl nipecotinate and ethyl-β-chloropropionate or from nipecotinic acid and β-chloropropionic acid, has b. p. 159—161°/5 mm., d_{20}^{20} 1·0452, n_D^{18} 1·4605. *Ethyl* iso*granatoninecarboxylate hydrochloride* forms white, microscopic crystals, m. p. 187—189°; it is extremely soluble in water and gives a deep reddish-purple coloration with ferric chloride. The keto-ester hydrochloride can be obtained crystalline by adding dry ether to its alcoholic solution until a faint cloudiness appears and then cooling to about −12°. *Ethyl* iso*granatoninecarboxylate* is a thick, colourless oil, b. p. 137—139°/8 mm., d_{20}^{20} 1·1381, n_D^{18} 1·5070; it gives a pronounced colour with acidified ferric chloride solutions. *Ethyl* iso*granatolinecarboxylate hydrochloride*, obtained by the reduction of the ketone with sodium amalgam in acid solution or by catalytic reduction in alcoholic solution in the presence of the platinum oxide catalyst, melts at 199—201°. An *isomeride* appears to be present in the mother-liquors left after crystallisation. The *benzoyl* derivative of the alcohol is obtained in the form of its hydrochloride as a white, crystalline powder.

An ethereal solution of the crude keto-ester (II) gradually deposits crystals which from their solubility in organic solvents probably consist of compound (III). F. G. P.

Pepper-substances. III. The Chavicine of Black Pepper. II. E. Ott and O. Lüdemann (*Ber.*, 1924, **57**, [*B*], 214—216).—Chavicine is purified by dissolution in benzene, addition of stannic

bromide, and precipitation of the additive compound (as a resinous mass) by means of ether. Analysis of the chavicine, regenerated after further dissolution in benzene and precipitation with ether, confirms the previous conclusion (Ott and Eichler, A., 1922, i, 1026) that it is stereoisomeric with piperine. Treatment of purified chavicine with alcoholic alkali hydroxide solutions yields unchanged material, *iso*chavicic acid, and piperidine; wax alcohols and fatty acids are not produced as is the case when crude chavicine is employed. H. W.

Ester Condensations with Ethyl *o*-Aminophenylacetate and Oxindole. W. Wislicenus and H. Bubeck (*Annalen*, 1924, **436**, 113—124).—It was expected that by condensing ethyl *o*-aminophenylacetate (Neber, A., 1922, i, 545) with ethyl formate, indole-3-carboxylic acid would be formed, but actually the product was oxindole-3-aldehyde (Friedländer, A., 1910, i, 592). Ethyl oxalate with the amino ester gave ethyl 2 : 3-dihydroxycinchoninate,

$$C_6H_4\!<\!\begin{matrix}C(CO_2Et):C\cdot OH\\ NH\text{———}CO\end{matrix},$$

together with a little oxindole-3-glyoxylic ester. Oxindole-3-aldehyde, obtained as above or from oxindole itself, forms yellow needles, m. p. 205—206°, and its anil has m. p. 254°. *Oxindole-3-glyoxylic acid*, the ester of which was obtained by condensing oxindole and ethyl oxalate, forms orange-yellow leaflets, m. p. 262—265° (decomp.); *anilide*, yellow leaflets, m. p. 261° (decomp.). The *ethyl* ester crystallises in orange needles, m. p. 187—188°, gives a green, crystalline *copper* salt, a *benzoyl* derivative (yellow needles, m. p. 160—161°), an *anil* (yellow prisms, m. p. 191—193°), and the corresponding *compound* with α-naphthylamine (m. p. 190°). Titration with bromine indicates that ethyl oxindole-3-glyoxylate exists solely in the *enolic* form. When treated with phenylhydrazine, it gives a mixture of the *phenylhydrazide* of the acid (needles, m. p. 238—239°) and the *phenylhydrazone* of the ester (yellow prisms, m. p. 160—164°), but at higher temperatures a *substance*, $C_{16}H_{11}O_2N_3$, crystallising in colourless needles, which decomposes at 265°. The *phenylmethylhydrazone* of the ethyl ester forms yellowish-brown prisms, m. p. 139°. *Methyl oxindole-3-glyoxylate* forms yellow needles, m. p. 167—169° (decomp.), and gives a *phenylhydrazone*, m. p. 197° (decomp.), which again gives the above compound, $C_{16}H_{11}O_2N_3$, when boiled with glacial acetic acid.

Ethyl 2 : 3-*dihydroxycinchoninate* forms needles, sintering about 210°, melting at 227—228°, and decomposing at 230°. It is a weak acid, giving crystalline ammonium and hydrazine salts. The *acid* forms white needles and decomposes without melting at 180°, giving 2 : 3-dihydroxyquinoline (Madelung, A., 1913, i, 92). Its *anilide* forms needles, m. p. 260° (decomp.). The *benzoyl* and *acetyl* derivatives of the ester (only the 3-hydroxy group reacted in each case) melt at 182—183° and 190°, respectively. W. A. S.

[Tri-indolylmethanes and Aldehydes, Ketones, Ketonic Esters, and Keto-nitriles of Substituted Indoles.] H. FISCHER (*Ber.*, 1924, **57**, [*B*], 356).—2-Methylindole-3-aldehyde (cf. Fischer and Pisbor, this vol., i, 86) has been obtained previously by Barger (A., 1917, i, 476). H. W.

Mechanism of Diazo Coupling Reactions. IV. Azo Dyes from 2-Methylenetrialkylindolines. W. KÖNIG and J. MÜLLER (*Ber.*, 1924, **57**, [*B*], 144—149; cf. A., 1923, i, 862).—2-Methylene-1 : 3 : 3-trialkylindolines couple with diazonium salts to yield azo dyes whereby the alkyl group in position 1 is removed as the corresponding alcohol. The new compounds are of the general type, $\left.\begin{matrix}\text{C}\\ \text{C}_6\text{H}_4\text{—NH}\end{matrix}\right\rangle$(Alk)$_2$·C:CH·N:NAr, which becomes somewhat modified when a chromophoric group is present in the para-position in the diazonium component. The facility with which coupling occurs depends on the nature of the 3-alkyl groups.

The following compounds are described: 1 : 2 : 3 : 3-*Tetramethylindoleninium bromide*, pale yellow crystals, m. p. 252° (decomp.), and the corresponding *perchlorate*, long, colourless needles, m. p. 192° (decomp.). 2-Methyl-1 : 3 : 3-triethylindoleninium *picrate*, yellow needles, m. p. 180°, and the very hygroscopic *chloride*, slender, colourless needles, m. p. 131°. 1 : 2-*Dimethyl*-3 : 3-*diethylindoleninium picrate*, dark yellow needles, m. p. 167° (the corresponding *chloride* and *perchlorate* are extremely hygroscopic). 2 : 3 : 3-*Trimethyl*-1-*ethylindoleninium perchlorate*, needles, m. p. 197° (decomp.).

2-Benzeneazomethylene-3 : 3-dimethylindoline is isolated as the *hydrochloride*, $C_{17}H_{18}N_3Cl$, m. p. 186° (decomp.), by treatment of a solution of 1 : 2 : 3 : 3-tetramethylindolinium iodide (or bromide) with sodium hydroxide and addition of benzenediazonium chloride to the emulsion of the methylene base. 2-p-*Nitrobenzeneazomethylene*-3 : 3-*dimethylindoline*, prepared in a similar manner from 2-methylene-1 : 3 : 3-trimethylindoline or 2-methylene-1-ethyl-3 : 3-dimethylindoline, crystallises in reddish-brown leaflets, m. p. 168°; the corresponding *hydrochloride*, brownish-red needles, decomp. about 286°, the *hydrobromide*, brownish-red needles, decomp. 250°, and the *acetate*, leaflets, are described. 2 : 4′-*Nitro*-2′-*methoxybenzeneazomethylene*-3 : 3-*dimethylindoline* forms lustrous, steel-blue needles, m. p. 211° (*hydrochloride* [+CH_3·CO_2H], m. p. 128°, and subsequently decomp. about 290°). 2-*p*-Nitrobenzeneazomethylene-3 : 3-diethylindoline could not be caused to crystallise; the *hydrochloride*, brownish-yellow needles, has m. p. 280° (decomp.). 2-p-*Acetylbenzeneazomethylene*-3 : 3-*dimethylindoline* crystallises in lustrous, red needles, m. p. 191°; the *hydrobromide* forms reddish-brown needles, m. p. 264°. H. W.

Supposed Syntheses from Ethyl Isatin-1-carboxylate. A. HANTZSCH (*Ber.*, 1924, **57**, [*B*], 195—199).—A criticism of the work of Heller (A., 1918, i, 309). Heller's 2 : 3-dihydroxy-2 : 3-dihydroindole-2-carboxylic acid is shown to be formylisatoic acid, CHO·NH·C_6H_4·CO·CO_2H, since its production from ethyl isatin-

1-carboxylate by the action of warm water or cold sulphuric acid (50%) is accompanied by that of acetaldehyde whilst, also, it is hydrolysed in alkaline solution to isatoic and formic acids; this conclusion is confirmed by the analysis of the ethyl ester, m. p. 67°. The supposed "lactone-like anhydride," m. p. 108°, is proved to be 1-formylisatin, since its optical properties are almost identical with those of 1-acetylisatin; attempts to prepare it directly from isatin and formic acid in the presence of dehydrating agents were, however, unsuccessful. Heller's 2 : 4-dihydroxy-1 : 2 : 3 : 4-tetrahydroquinoline-2-carboxylic acid is, in reality, formylanthranilic acid, which is transformed by acetic anhydride and sodium acetate into acetylanthranilic acid (Heller's hydroxydihydroquinoline-2-carboxylic acid, m. p. 184°). The observed formation of yellow solutions of the colourless formylisatoic acid in water and anhydrous solvents is due to the ready production of 1-formylisatin. H. W.

Catalytic Hydrogenation of Pyridine. N. Zelinsky and P. Borisoff (*Ber.*, 1924, **57**, [*B*], 150—153).—Pyridine is very readily hydrogenated to piperidine in the presence of platinised asbestos (40%) at 150°. The catalyst does not become poisoned, since it retains its ability to cause the hydrogenation of benzene. At about 250°, it smoothly effects the dehydrogenation of piperidine, but, after use, it is no longer capable of bringing about the reduction of benzene or pyridine or the dehydrogenation of *cyclo*hexane. Palladised asbestos is a still more effective agent for the hydrogenation of pyridine at 150°; after use, however, it is found to have lost all activity towards benzene. It readily causes the dehydrogenation of piperidine, but not of *cyclo*hexane at 250°; after use, it is incapable of effecting hydrogenation.

The preparation of the highly active catalyst is effected in the following manner. Asbestos, which has been washed with acid and ignited, is soaked in a concentrated, faintly acid solution of platinum or palladium chloride at the temperature of boiling water and subsequently immersed in cold formaldehyde solution (35—40%). It is then treated with concentrated sodium hydroxide solution (40—50%), initially at 0° and finally on the water-bath. The product is washed thoroughly with water, immersed in dilute acetic acid solution, and again washed until the filtrate is neutral in reaction. It is dried for a short period at 110°. H. W.

Complex [Pyridine, Pyrazine, and Quinoxaline] Salts of Bivalent Iron. H. Ley, C. Schwarte, and O. Münnich.—(See ii, 228.)

The Product of the Action of Acidic Reducing Agents on Indigotin. W. Madelung and P. Siegert (*Ber.*, 1924, **57**, [*B*], 222—233).—The reduction of indigotin in the presence of acids leads to the opening of the ring with formation of 2 : 2′-diamino-ω-styrylacetophenone.

The gradual addition of indigotin and finely-divided iron to an almost saturated solution of hydrogen chloride in alcohol leads to the separation of 2 : 2′-*diamino-ω-styrylacetophenone hydrochloride*, $NH_2 \cdot C_6H_4 \cdot CO \cdot CH_2 \cdot CH{:}CH \cdot C_6H_4 \cdot NH_2,HCl$, pale brown

crystals; the corresponding *picrate*, *sulphate*, and perchlorate are described. The hydrochloride is converted by acetic anhydride in the presence of pyridine into the *acetyl* derivative, $C_{20}H_{20}O_3N_2$, colourless leaflets, m. p. 181° (the *perchlorate* is described). With formaldehyde and benzaldehyde, respectively, the base gives the *compounds*, $C_{17}H_{16}ON_2$, greenish-yellow crystals, and $C_{23}H_{20}ON_2$, slender, greenish-yellow crystals. The conversion of indigotin into 2 : 2′-diamino-ω-styrylacetophenone can be effected by ferrous chloride or by the addition of indigo-white to alcoholic hydrogen chloride, whereby disproportionation occurs accompanied by precipitation of indigotin.

2 : 2′-Diamino-ω-styrylacetophenone is very easily dehydrogenated. The hydrochloride is converted by solution in warm pyridine and exposure to air into 2-o-*aminostyrylindoxyl*, $C_6H_4<\begin{matrix}C(OH)\\NH\end{matrix}>C\cdot CH:CH\cdot C_6H_4\cdot NH_2$, small needles, m. p. 161°, which is readily oxidised further; it gives a *monoacetyl* derivative, decomp. above 250°. Deoxyindigotin,

$$C_6H_4<\begin{matrix}CO\\NH\end{matrix}>C:C<\begin{matrix}CH_2\\NH\end{matrix}>C_6H_4$$

(cf. Borsche and Meyer, A., 1922, i, 55), is also obtained by the action of air on solutions of 2 : 2′-diamino-ω-styrylacetophenone in pyridine and is the sole product of the action of alcoholic solutions of potassium hydroxide or sodium alkoxide on the base. The ultimate product of the dehydrogenation of 2 : 2′-diamino-ω-styrylacetophenone is the *substance*, $C_6H_4<\begin{matrix}CO\\N\end{matrix}>C\cdot C<\begin{matrix}CH\\NH\end{matrix}>C_6H_4$, cocoa-brown, rhombic leaflets (*monoacetyl* derivative, pale yellow leaflets, decomp. 245—250°). When its solution in pyridine is exposed to air for 3—4 days the dimeric *compound*, $(C_{16}H_{10}ON_2)_2$, separates in the form of dark violet-blue, slender needles. A second dimeric *compound*, $(C_{16}H_{10}ON_2)_2$, is obtained by the action of concentrated acids on a solution of the monomeric substance, $C_{16}H_{10}ON_2$; the latter, which forms orange crystals, is immediately coloured green, probably owing to the formation of an unstable salt, and subsequently rapidly passes into the tile-red salt of the dimeride, which can also be obtained by dehydrogenation or disproportionation from the compounds $C_{16}H_{16}ON_2$, $C_{16}H_{14}ON_2$, and $C_{16}H_{12}ON_2$. It has well-marked basic properties and gives sparingly soluble salts with mineral acids, the most characteristic of which is the *hydriodide*, $C_{32}H_{20}O_2N_4,HI$. The *diacetyl* derivative, $C_{36}H_{24}O_4N_4$, is a red, crystalline powder. When boiled with an alcoholic solution of formaldehyde, the base is converted into the *substance*, $C_{33}H_{22}O_2N$ (orange-yellow crystals), whereas it is transformed by a boiling solution of sodium methoxide in methyl alcohol into the *compound* $C_{32}H_{28}O_2N_4$, canary-yellow, rhombic leaflets. H. W.

Imines, Anils, and Hydrazones of Indigotin and the Stereochemical Configuration of the Indigoids. W. Madelung and O. Wilhelmi (*Ber.*, 1924, **57**, [*B*], 234—241).—The carbonyl and imino groups of indigotin are so indifferent towards

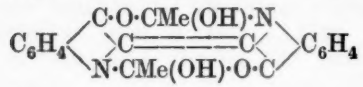
the usual reagents that their presence cannot be established in the customary manner. On the other hand, derivatives such as the oximes, phenylhydrazones, and azines can easily be prepared when di-iminoindigotin (Madelung, A., 1913, i, 904) is used as initial material; of these, indigotindioxime has already been described (Madelung, A., 1914, i, 738). The stability of indigotin suggests that there is an intimate connexion between the carbonyl and imino groups such as has been indicated by the constitutions proposed by Claasz (A., 1916, i, 840) and by Lifschitz and Lourié (A., 1917, i, 586). These formulæ do not, however, appear to be satisfactory, since they are valid only for indigotin itself, and cannot be extended to the derivatives of it which are now described; these are very closely related (optically) to indigotin. It is suggested that the oxygen atom of the carbonyl group is joined by a subsidiary valency either to the hydrogen atom of the imino group in the opposite half of the molecule, thus yielding a new six-membered ring, as has been proposed by Scholl (Georgievics, "Die Biziehungen zwischen Farbe u. Konstitution von Farbstoffen," 1920), or to the imino nitrogen atom, thus giving a new five-membered ring.

Indigotinbisphenylhydrazone, $C_{16}H_{10}N_2(:N\cdot NHPh)_2$, red needles, m. p. 219—220° (decomp.), is prepared by the gradual addition of phenylhydrazine to a solution of di-iminoindigotin acetate in glacial acetic acid and subsequent treatment of the hot saturated solution of the product in alcohol with anhydrous potassium carbonate; it separates from acetic acid in green crystals ($+2CH_3\cdot CO_2H$), m. p. 202—204°. The *hydrochloride*, $C_{28}H_{22}N_6,HCl$, green needles, and the *picrate*, $C_{28}H_{22}N_6,2C_6H_3O_7N_3$, green needles, are described. In a similar manner, di-iminoindigotin acetate is converted by hydrazine hydrate into *indigotinazine acetate*, $C_{16}H_{10}O_4,C_2H_4O_2$, long, somewhat unstable needles, m. p. above 300° after previous change; the free base is too unstable to isolate. *Indigotindianilide acetate*, $C_{28}H_{20}N_4,C_2H_4O_2$, dark, bluish-green crystals, is obtained from di-iminoindigotin acetate, aniline, and glacial acetic acid in boiling alcoholic solution; when dissolved in xylene and treated with anhydrous sodium carbonate, it gives the corresponding free base (cf. Grandmougin and Dessoulavy, A., 1910, i, 73). *Dimethyliminoindigotin acetate*, prepared from di-iminoindigotin acetate and methylamine in boiling alcoholic solution, has m. p. 252—254°; the corresponding *base* crystallises in blue needles. The action of acetic anhydride on the imino acetate affords *diacetyliminoindigotin*, aggregates of dark blue needles, m. p. 202°.

Indoleazobenzene, $C_{11}H_{11}N_3$, yellowish-brown crystals, m. p. 133—134°, is prepared by the gradual addition of a methyl-alcoholic solution of indole to an alkaline solution of diazotised aniline. H. W.

Alkyl and Acyl Derivatives of Leuco-indigotin and Indoxyl. W. Madelung (*Ber.*, 1924, **57**, [*B*], 241—252).—A study of the action of benzyl chloride on alkaline solutions of leuco-indigotin leads the author to the conclusion that, contrary to previous views, alkylation leads primarily to the production of *C*-substituted derivatives which readily undergo fission to substituted indoxyls. The

formation of two diacetyl-leuco-indigotins is very difficult to interpret; it is suggested that the acetyl groups are not present as such but form a bridge between the hydroxy and imino groups as indicated in the annexed formula. The stereoisomerism is due to the presence of two asymmetric carbon atoms in the two new rings (cf. Madelung and Hagen, A., 1916, i, 840).



[With O. HALLER.]—Indigo white is converted by methyl sulphate in the presence of sodium hydroxide into a dimethyl derivative, rhombic leaflets, m. p. above 235° (decomp.) after darkening at 200° (cf. Grandmougin, A., 1922, i, 470); it gives a *picrate*, dark violet needles, m. p. 173°, and is converted by nitrous acid in the presence of glacial acetic acid into indigotin.

Monobenzyl-leuco-indigotin, $C_{23}H_{18}O_2N_2$, ochre-yellow needles, m. p. 183°, is prepared by the action of benzyl chloride on leuco-indigotin at the ordinary temperature. When an excess of benzyl chloride is used under similar conditions, two isomeric *dibenzyl-leuco-indigotins* are formed. The main product, pale greenish-yellow crystals, m. p. 203°, resembles the dimethyl compound in yielding fluorescent solutions; it is unstable in hot solutions in the presence of acids. It is regarded as the *C*-dibenzyl compound, $C_6H_4<^{CO}_{NH}>C(CH_2Ph)\cdot C(CH_2Ph)<^{CO}_{NH}>C_6H_4$. The second substance, colourless needles, m. p. 192°, is stable in organic media, but more sensitive towards permanganate than its isomeride; it is considered to be the dibenzyl ether of leuco-indigotin. The substance, m. p. 203°, is converted by boiling glacial acetic acid into benzylideneindoxyl, $C_{15}H_{11}ON$.

When treated in alkaline solution with an excess of benzyl chloride at 70—80°, leuco-indigotin suffers fission and the primary products become further benzylated, whereby 2 : 2′-dibenzylindoxyl, yellow crystals, m. p. 174—175° (*nitroso* derivative, pale yellow, lustrous leaflets, m. p. 135°), and 2-*benzylindoxyl benzyl ether*, colourless, slender needles, m. p. 198—199°, are formed; the latter substance is readily oxidised by permanganate, but is stable towards nitrous acid.

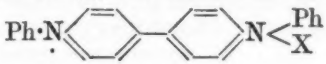
1-Acetylindoxyl gives a *phenylhydrazone*, $C_{16}H_{15}ON_3$, pale yellow needles, m. p. 154°, and an *oxime hydrochloride*, $C_{10}H_{10}O_2N_2$,HCl, colourless needles, m. p. 139°.

Indigotin is converted when heated with acetic anhydride, zinc dust, and acetyl chloride into a *compound*, $C_{20}H_{14}O_3N_2$, yellow needles, m. p. 209—210°, which is regarded as *diacetylanhydroleuco-indigotin*; the success of the preparation depends greatly on the purity of the materials and appears to be governed largely by experimental conditions. H. W.

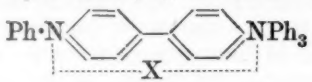
Spectroscopy of the Sulphonated Indigotins. W. C. HOLMES (*J. Amer. Chem. Soc.*, 1924, **46**, 208—214).—The absorption spectra of the pure potassium salts of sulphonated indigotin in the visible spectrum have been measured under various conditions. The absorption maxima of the potassium salts in aqueous solution were :

monosulphonate, 608 $\mu\mu$; disulphonate, 610 $\mu\mu$; trisulphonate, 603 $\mu\mu$; tetrasulphonate, 590 $\mu\mu$. Data are supplied for their spectrophotometric identification and evaluation. F. A. M.

Free Ammonium Radicals. V. Comparison of 1 : 1′-Dibenzyl- and 1 : 1′-Diphenyl-4 : 4′-dipyridinium. E. WEITZ, T. KÖNIG, and L. VON WISTINGHAUSEN (*Ber.*, 1924, **57**, [*B*], 153—175).—Further insight into the constitution of pyridinium radicals is obtained by a study of the reduction of 1 : 1′-diphenyl-4 : 4′-dipyridinium iodide, which has led to the isolation of deeply coloured compounds containing an atom of iodine united with a molecular proportion of the radical. The relationships are similar, but less obvious in the benzyl series (cf. Weitz and König, A., 1922, i, 1186). Compounds of this type are formulated by the authors as semi-radicals (I), or intramolecular quinhydrones (II), whereas they



(I.)



(II.)

have been regarded by Emmert (A., 1922, i, 1064) and Dimroth (A., 1923, i, 149) as quinhydrone-like products of the union of molecular proportions of the radical and the dihalogenide.

1 : 1′-Dibenzyl-4 : 4′-dipyridinium subiodide (cf. Emmert and Varenkamp, A., 1922, i, 1064) is obtained by the reduction of the di-iodide with metals or, more conveniently, by the action of the di-iodide on the radical; it crystallises in coarse platelets with a metallic reflex, m. p. about 190°, according to the rate of heating. It is reduced to the free radical by metallic sodium or an excess of dibenzyldipyridinium in alcoholic solution. The corresponding sub-chloride is isolated in blackish-violet, rhombohedral crystals, m. p. about 190° when rapidly heated; the molecular weight in boiling methyl alcohol is about half that required by the formula, $C_{24}H_{22}N_2Cl$.

1-Phenylpyridinium chloride, m. p. 105° (corresponding *per-chlorate*, colourless needles, m. p. 221°), is conveniently prepared by boiling the so-called " pyridine dye " (from dinitrophenylpyridinium chloride or pyridine cyanobromide and aniline) with alcohol and concentrated hydrochloric acid and addition of ferric chloride solution; the additive salt, $C_{11}H_{10}NCl,FeCl_3$, is subsequently decomposed by the requisite amount of sodium carbonate. It is reduced by sodium amalgam in aqueous solution mainly to *1-phenyl-*$\Delta^{1\cdot4}$(?$\Delta^{1\cdot2}$)*-dihydropyridine*, transparent crystals, m. p. 49—50° (the constitution of which is deduced from its properties, its molecular weight, and its conversion by iodine into 1-phenylpyridinium iodide); *bis-1-phenylpyridinium* [*1 : 1′-diphenyltetrahydro-4 : 4′-dipyridyl*], $Ph\cdot N<\begin{matrix}CH{:}CH\\CH{:}CH\end{matrix}>CH\cdot CH<\begin{matrix}CH{:}CH\\CH{:}CH\end{matrix}>N\cdot Ph$, silvery leaflets, m. p. 136° (decomp.) after darkening at 100° when rapidly heated, is produced in minor amount. If, however, the reduction is effected in permanently neutral or faintly acid solution (for example, by sodium amalgam in the presence of aluminium sulphate), the leuco compound is alone formed; on the other hand, the dihydro product

is almost exclusively produced if the solution is made alkaline from the commencement of the experiment. The action of iodine on 1 : 1′-diphenyltetrahydro-4 : 4′-dipyridyl proceeds in a complex manner, yielding 1 : 1′-diphenyl-4 : 4′-dipyridinium di-iodide, red prisms, m. p. about 360° (cf. König, A., 1923, i, 382); the corresponding perchlorate and picrate have m. p. 311° and 244°, respectively, whereas König (*loc. cit.*) gives m. p. 299° and 170°; *1-phenylpyridinium iodide*, colourless, flattened prisms or anhydrous leaflets, m. p. 210° after darkening above 100°, is also produced, whilst about half the original material remains in the chloroform.

1 : 1′-*Diphenyl*-4 : 4′-*dipyridinium*, Ph·N N·Ph, is most conveniently prepared by dissolving 1 : 1′-diphenyltetrahydro-4 : 4′-dipyridyl in a warm mixture of pyridine and methyl alcohol and preserving the mixture in a closed, half-filled flask for about a week; it separates from the solution in red, rhombic crystals with a vivid blue reflex, decomp. above 180°. It decomposes readily when exposed to air. It is converted by iodine in all solvents with the exception of benzene, primarily into the subiodide (below) and finally into the red di-iodide. The radical may also be prepared by the reduction of an aqueous solution of the di-iodide with zinc dust. 1 : 1′-*Diphenyl*-4 : 4′-*dipyridinium subiodide*,

$$Ph{\cdot}C_5H_5N{\cdot}C_5H_5NPhI,$$

is most conveniently prepared by mixing equivalent quantities of diphenyldipyridinium di-iodide and the corresponding leuco compound dissolved in acetone or chloroform; it crystallises in lustrous, steel-blue prisms, m. p. 318—319° (decomp.).

1 : 1′-Diphenyltetrahydro-4 : 4′-dipyridyl dissolved in chloroform is converted by a mixture of oxygen and carbon dioxide into 1 : 1′-*diphenyl*-4 : 4′-*dipyridinium hydrogen subcarbonate*, short prisms which appear violet by reflected, nearly black by transmitted light. The product is also obtained when a mixture of nitric oxide and carbon dioxide is used. H. W.

Cyclic Di-imines and their Decomposition. III. J. von Braun, G. Blessing, and F. Zobel (*Ber.*, 1924, **57**, [*B*], 185—191; cf. A., 1923, i, 840).—The catalytic hydrogenation of γ-phenoxy-*n*-butyronitrile in amyl-alcoholic solution (cf. A., 1923, i, 1088) gives a mixture of δ-phenoxybutylamine and di-δ-phenoxybutylamine; when subjected to slow distillation, the secondary base is transformed into phenol and *phenoxybutylpyrrolidine*, a colourless liquid, b. p. 170°/13 mm. (the hygroscopic *hydrochloride*, the *picrate*, yellow needles, m. p. 110°, and the *methiodide*, m. p. 123°, are described). It is converted by fuming hydrobromic acid at 100° into δ-*bromobutylpyrrolidine* (identified as the *chloroplatinate*, m. p. 133—134° after softening at about 130°), which is readily transformed into dipyrrolidinium bromide (cf. von Braun, A., 1916, i, 631). The salt is slowly converted by concentrated ammonia at 170—180° into ditetramethylenedi-imine,

$$\begin{matrix} CH_2{\cdot}CH_2{\cdot}NH{\cdot}CH_2{\cdot}CH_2 \\ | \qquad\qquad\qquad\qquad | \\ CH_2{\cdot}CH_2{\cdot}NH{\cdot}CH_2{\cdot}CH_2 \end{matrix},$$

a colourless liquid, b. p. 95°/12 mm., d_4^{18} 0·902; the hygroscopic *hydrochloride*, the *chloroplatinate*, yellowish-red crystals, decomp. 207°, the *picrate*, m. p. 203—204°, the *benzenesulphonyl* compound, the *nitroso* derivative, the exceedingly hygroscopic *dimethiodide*, and the corresponding *chloride* and *chloroplatinate*, decomp. 257°, are described.

Tetramethylenepentamethylenedi-imine, a liquid, b. p. 110—112°/14 mm., d_4^{11} 0·920, is prepared similarly from the corresponding bromide; it yields a non-crystalline *benzenesulphonyl* derivative and *picrate*, a hygroscopic *hydrochloride*, a *chloroplatinate*, decomp. 190°, and a *di-methiodide*, $C_{13}H_{30}N_2I_2$, m. p. 247°, which is transformed through the *chloride* into the corresponding *chloroplatinate*, decomp. 248°.

Treatment of dipiperidinium bromide with aqueous ammonia (cf. A., 1907, i, 151) leads to the isolation of very small yields of *dipentamethylenedi-imine* (*dipiperidine*), b. p. 108—110°/12 mm., d_4^{17} 0·9195. The non-crystalline *picrate* and *nitroso* derivative, the hygroscopic *hydrochloride*, and the *chloroplatinate*, an orange-coloured, crystalline powder, decomp. 180°, are described. The *dimethiodide*, m. p. 272° (decomp.), and the corresponding *chloroplatinate*, decomp. 247°, have been prepared. H. W.

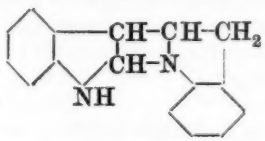
Discatole. B. Oddo and G. B. Crippa (*Atti R. Accad. Lincei*, 1924, [v], **33**, i, 31—34).—*Discatole*, $C_{18}H_{18}N_2$, obtained as hydrochloride by subjecting scatole, in anhydrous ethereal solution, to the action of a slow current of hydrogen chloride, forms white needles, m. p. 130°, and is free from the fæcal odour of scatole itself. Its *hydrochloride*, $C_{18}H_{18}N_2,HCl$, forms microscopic, highly refractive, prismatic crystals, m. p. 173°; its orange-red *picrate*,

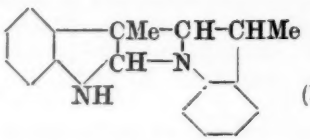
$$C_{18}H_{18}N_2,C_6H_3O_7N_3,$$

m. p. 170°, and its colourless *oxalate*, $(C_{18}H_{18}N_2)_2,C_2H_2O_4$, m. p. 180°, are described. It has not been found possible to obtain a triscatole.

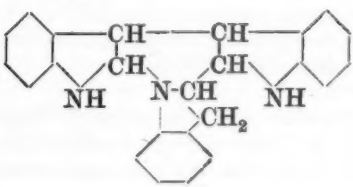
These results, in conjunction with the facts that indole gives both a dimeride and a trimeride, that 2-methylindole undergoes no such polymerisation, and that any of these polymerides yields only a mono-hydrochloride, indicate for di-indole, discatole, and tri-indole the formulæ (I), (II), and (III), respectively:

(I.)





(II.)



(III.)

T. H. P.

Dyes derived from Acenaphthenequinone. A. C. SIRCAR and S. K. GUHA (*J. Chem. Soc.*, 1924, **125**, 335—340).—Azines produced by the condensation of acenaphthenequinone and of its 3 : 4-dinitro derivative with *o*-diamines, possess tinctorial properties not inferior to those of the corresponding derivatives of phenanthraquinone. Although insoluble in water, they can be used when freshly precipitated for dyeing wool. The azine sulphonic acids and azonium derivatives are also satisfactory dyestuffs. The reduction products of the 3 : 4-dinitroazines have probably the diaminodihydroazine structure (cf. T., 1922, **121**, 1950). Attempts to prepare 3-nitroacenaphthenequinone by the method of Rowe and Davies (T., 1920, **117**, 1349) always yielded a product containing the dinitro derivative. The following substances are described: *acenaphthatolazine*, $C_{12}H_6\langle\overset{N}{N}\rangle C_6H_3Me$, light brown needles, m. p. 232°. *Acenaphthanaphthazine*,

$$C_{12}H_6\langle\overset{N}{N}\rangle C_{10}H_6,$$

brownish-yellow needles, m. p. 290°. *3 : 4-Dinitroacenaphthatolazine*, $(NO_2)_2C_{12}H_4\langle\overset{N}{N}\rangle C_6H_3Me$, orange-yellow needles, m. p. not below 290°. 3 : 4-*Dinitroacenaphthanaphthazine*,

$$(NO_2)_2C_{12}H_4\langle\overset{N}{N}\rangle C_{10}H_6,$$

scarlet-red, shining needles, m. p. not below 290°. 3 : 4-*Dinitroacenaphthaphenazine*, $(NO_2)_2C_{12}H_4\langle\overset{N}{N}\rangle C_6H_4$, orange-yellow plates, m. p. not below 290°. 3 : 4-*Dinitroacenaphthaphenazinazine*, $(NO_2)_2C_{12}H_4\langle\overset{N}{N}\rangle C_6H_2\langle\overset{N}{N}\rangle C_6H_4$, red, prismatic needles, no m. p. *Acenaphthanaphthazine-5′-sulphonic acid*, $C_{12}H_6\langle\overset{N}{N}\rangle C_{10}H_5\cdot SO_3H$, microscopic, brownish-yellow needles, m. p. not below 300°. 3 : 4-*Dinitroacenaphthanaphthazine-5′-sulphonic acid*, brown, amorphous precipitate. *Phenylacenaphthanaphthazonium chloride*,

$$C_{12}H_6\langle\overset{N}{NPhCl}\rangle C_{10}H_6,$$

greenish-black powder, m. p. not below 290°. *Phenyl-3 : 4-dinitroacenaphthanaphthazonium chloride*, similar, m. p. 270°. *Naphthylacenaphthaphenazonium chloride*, dull, black powder, m. p. not below 290°. 3 : 4-*Diamino-7 : 12-dihydroacenaphthaphenazine*,

$$(NH_2)_2C_{12}H_4\langle\overset{NH}{NH}\rangle C_6H_4,$$

orange-red prisms, m. p. (with sublimation) above 290°. 3 : 4-*Diamino-7 : 12-dihydroacenaphthanaphthazine*, scarlet-red, rectangular plates. 3 : 4-*Dihydroxy-7 : 12-dihydroacenaphthaphenazine*, brick-red powder, subliming above 290°. F. G. W.

Action of Hydrazine on Uracil and Thymine. R. FOSSE, A. HIEULLE, and L. W. BASS (*Compt. rend.*, 1924, **178**, 811—813).—Uracil reacts with hydrazine to give carbamide and pyrazolone,

the latter with xanthhydrol affording 1 : 2- or 1 : 4-*dixanthylpyrazolone*, colourless filaments, colouring at 195° and melting at 210—213° to a red liquid. Thymine, treated successively with hydrazine hydrate and xanthhydrol, affords dixanthylcarbamide and *dixanthyl*-4-*methylpyrazolone* (colourless crystals, m. p. about 202°), this substance also resulting by the action of xanthhydrol on the crude condensation product from hydrazine and ethyl formylpropionate. E. E. T.

Oxidation Products of Bilirubin. Detection of Urobilin. A. ADLER.—(See ii, 280.)

5-Nitrobarbituric Acids. H. BILTZ and K. SEDLATSCHECK (*Ber.*, 1924, **57**, [*B*], 339—349).—Violuric acid, decomp. 240—241° after darkening at 220° (cf. Biltz and Hamburger, A., 1916, i, 505) is converted by concentrated nitric acid into 5-nitrobarbituric acid, decomp. 180—181°, the yield being about 95% of that theoretically possible. The latter acid when suspended in ice-cold water and treated with chlorine yields *5-chloro-5-nitrobarbituric acid*, $CO<^{NH\cdot CO}_{NH\cdot CO}>CCl\cdot NO_2$, colourless, slender needles, decomp. 86—87°, which is decomposed by warm water into nitrobarbituric acid, carbamide, and chloropicrin and by bleaching powder solution into chloropicrin and carbamide. *5-Bromo-5-nitrobarbituric acid*, long, slender needles, decomp. 108°, is decomposed by warm water in the same manner as the chloro compound. The position of the halogen atom in these acids is established by the observation that they are transformed by diazomethane into 5-halogeno-5-nitro-1 : 3-dimethylbarbituric acids (see later).

5-*Nitro*-1-*methylbarbituric acid*, $C_5H_5O_5N_3,2H_2O$, colourless, slender needles, decomp. 142—143°, is prepared in 92% yield from methylvioluric acid; the *ammonium*, *potassium*, *sodium* ($+H_2O$), and *barium* ($+H_2O$) salts are described. The acid is remarkably stable towards solutions of alkali hydroxides. *5-Chloro-5-nitro-1-methylbarbituric acid*, colourless, hexagonal plates, decomp. 122—123°, is decomposed completely by boiling water into nitromethylbarbituric acid, methylcarbamide, chloropicrin, and carbon dioxide. *5-Bromo-5-nitro-1-methylbarbituric acid* forms colourless, four-sided prisms, m. p. 137—138°.

5-Nitro-1 : 3-dimethylbarbituric acid, small, colourless needles, decomp. 148—149° (the sodium and *potassium* salts are described), is converted into 5-chloro-5-nitro-1 : 3-dimethylbarbituric acid, decomp. 150°, and 5-bromo-5-nitro-1 : 3-dimethylbarbituric acid, decomp. 152°.

5-*Nitro*-1-*ethylbarbituric acid*, $C_6H_7O_5N_3,H_2O$, forms colourless needles, decomp. 132—133°; the *ammonium*, *potassium*, *sodium*, *calcium*, and *strontium* salts are described. *5-Chloro-5-nitro-1-ethylbarbituric acid* crystallises in colourless, rhombic leaflets, decomp. 127—128°. *5-Bromo-5-nitro-1-ethylbarbituric acid* is a heavy, microcrystalline powder, decomp. 138—139°.

5-*Nitro*-1 : 3-*diethylbarbituric acid*, colourless octahedra, decomp. 116—117°, is prepared from diethylvioluric acid; it may also be

obtained in poorer yield by the direct nitration of 1 : 3-diethylbarbituric acid, whereby diethylalloxan and tetraethylalloxantin are also produced; the *ammonium* salt, long, colourless needles, is described. *5-Chloro-5-nitro-1 : 3-diethylbarbituric acid*, a heavy, crystalline precipitate, decomp. 53°, and *5-bromo-5-nitro-1 : 3-diethylbarbituric acid*, a heavy, micro-crystalline powder, decomp. 63—64°, have been prepared.

Evidence is adduced against the existence of violantin and its alkyl derivatives. H. W.

Acetonylbarbituric Acid and some of its Derivatives. A. W. Dox and B. Houston (*J. Amer. Chem. Soc.*, 1924, **46**, 252—256).—The acetonyl group may be introduced directly at carbon atom 5 of barbituric acid by means of chloroacetone. Further substitution by halogen is readily effected, or by allyl, benzyl, and acetonyl. The less reactive alkyl halides, such as butyl bromide, do not react readily with acetonylbarbituric acid, but the acetonyl and alkyl groups may be introduced in the reverse order by treatment of the monoalkylbarbituric acid with chloroacetone. The acetonylalkylbarbituric acids are much less effective as hypnotics than the dialkylbarbituric acids with the same length of side chains.

It was not found possible to prepare ethyl acetonylmalonate from sodiomalonic ester and chloroacetone, but barbituric acid itself was alkylated readily in boiling aqueous solution.

Acetonylbarbituric acid forms flat, yellow crystals, m. p. 238—240° (decomp.); it liberates acetic acid from its salts. Halogenation yielded respectively *acetonylbromobarbituric acid*, white needles, decomp. about 143° without melting, and *acetonylchlorobarbituric acid*, white needles, which begin to decompose about 175° and melt about 245°. The following dialkylated acids were prepared by further treatment of acetonylbarbituric acid in the usual manner: *diacetonylbarbituric acid*, white needles, m. p. 264—266° (decomp.), *acetonylallylbarbituric acid*, large, white crystals, m. p. 216—217°, *acetonylbenzylbarbituric acid*, large, prismatic crystals, m. p. 224—225°; *acetonylethylbarbituric acid*, flat, white crystals, m. p. 238—239°. F. A. M.

Velocity of Spontaneous Oxidation of Uric Acid in Alkaline Solution. L. Piaux (*Compt. rend.*, 1924, **178**, 637—640; cf. Biltz and Robl, A., 1920, i, 883, and More, this vol., i, 315).—An aqueous solution containing 5 mols. of potassium hydroxide to 1 mol. of uric acid rapidly absorbs oxygen; with a smaller porportion of base oxidation is less rapid. A considerable quantity of ammonia is formed. On acidifying, carbon dioxide is evolved, and addition of alcohol then causes the precipitation of potassium oxonate, $C_4H_2O_4N_3K$. The main reaction may be written thus: $C_5H_4O_3N_4 + O_2 + H_2O = CO_2 + NH_3 + C_4H_3O_4N_3$.

Since allantoin was not formed in these oxidation processes, the author examined the action of air (1) on an alkaline solution of potassium allantoate, and (2) on an alkaline solution of uric acid which had previously (by means of permanganate) been oxidised to the extent of 1 atom of oxygen. (Solution 2, according

to Biltz and others [*loc. cit.*] contains a substance which is oxidisable to an oxonate.) Neither (1) nor (2) absorbed oxygen.

E. E. T.

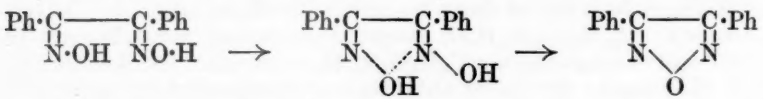
Action of Catalysts on the Oxidation of Uric Acid. Iron and Manganese (Hydroxides). L. Piaux (*Compt. rend.*, 1924, **178**, 782—785; cf. preceding abstract).—The aërial oxidation of uric acid (1 mol.) in potassium hydroxide (5 mols.) solution, is accelerated by traces of ferric hydroxide, potassium oxonate being formed. Manganese oxide hydrates (obtained by using manganese lactate) accelerate the initial aërial oxidation but diminish the amount of oxonate formed, none of the latter being obtained when 1 mol. of lactate is originally taken per 5·6 mols. of uric acid. Allantoin takes its place, and is formed from the intermediate compound described by Biltz and Behrend (cf. A., 1921, i, 893).

E. E. T.

Ethylated Uric Acids. H. Biltz and K. Sedlatschek (*Ber.*, 1924, **57**, [*B*], 175—182).—The action of ethyl bromide on dipotassium urate in the presence of carbon tetrachloride at 110° leads to the production of moderate yields (12—13%) of 3 : 7 : 9-triethyluric acid, colourless aggregates of needles, m. p. 204°; the product is probably identical with the triethyluric acid obtained by Drygin in 1864 by the action of ethyl iodide on lead urate. The constitution of the acid is deduced from its oxidative degradation to *diethylalloxantin*, $C_{12}H_{14}O_8N_4,H_2O$, large, transparent crystals, m. p. 209°, and 1-*ethylalloxan*, $C_6H_6O_4N_2,H_2O$, slender needles, m. p. 103° (decomp.); the latter substance is transformed by hydroxylamine hydrochloride into the previously described 1-ethylvioluric acid. Two of the ethyl groups of the triethyluric acid must therefore be present in the glyoxalone ring, that is, in positions 7 and 9, whilst the third must occupy position 3, since the alkylated compound is prepared from the solid potassium salt. As recorded by Drygin, when 3 : 7 : 9-triethyluric acid is warmed with concentrated hydrochloric acid, an ethyl group is eliminated as ethyl chloride and 3 : 7-*diethyluric* acid, slender, rhombic leaflets, m. p. 350—355°, is almost quantitatively produced; the same change occurs under the conditions of Zeisel's alkoxy determination. The presence of an ethyl group in position 3 is proved by oxidation of the acid to diethylalloxantin and ethylalloxan, m. p. 103°, whilst the second ethyl group necessarily occupies position 7, since fission of the acid with concentrated hydrochloric acid at 170° leads to the production of ethylglycine hydrochloride, which is identified by transforming it into 1-ethylhydantoin. 3 : 7 : 9-Triethyluric acid is readily converted by diazomethane in ethereal solution in the presence of a little water into 1-*methyl*-3 : 7 : 9-*triethyluric acid*, long, colourless needles, m. p. 104°. 1 : 3 : 7 : 9-*Tetraethyluric acid*, aggregates of slender needles, m. p. 82°, is prepared similarly with the aid of diazoethane. Treatment of the tetra-alkyl compounds with concentrated hydrochloric acid leads to the production of 1-*methyl*-3 : 7-*diethyluric acid*, feathery aggregates of needles, m. p.

257—258°, and 1 : 3 : 7-*triethyluric acid*, colourless needles, m. p. 218—219°. H. W.

The Beckmann Transformation. II. J. MEISENHEIMER and W. LAMPARTER (*Ber.*, 1924, **57**, [*B*], 276—282).—Reasons have previously been advanced (Meisenheimer, A., 1922, i, 152) in favour of a redistribution of formulæ among the benzildioximes whereby the α-dioxime receives the *anti*-, the β-dioxime the *syn*-, and the γ-dioxime retains the *amphi*-configuration. The tendency of the dioximes to lose water has been examined by heating in evacuated tubes at 155°; under these conditions, the α-dioxime is volatilised most slowly and with partial isomerisation to the β-dioxime; the latter sublimes more readily without undergoing decomposition, whereas only the γ-dioxime loses water and forms an anhydride; transformation into the β-dioxime accompanies the latter action and the formation of the anhydride ceases as soon as the isomerisation is complete. The behaviour of the oximes themselves is in harmony with that of their acetates, since the derivatives of the α- and β-forms are hydrolysed by cold sodium hydroxide solution to the corresponding oximes, whereas the diacetate of the γ-variety yields the anhydride. The behaviour of the dibenzoates exactly resembles that of the diacetates. The observations necessitate a new conception of the mechanism of anhydride formation, that represented in the following scheme being suggested:



Dibenzoyl-α-benzildioxime, prepared from the α-dioxime and benzoyl chloride in the presence of pyridine, crystallises in colourless needles, m. p. 220°; *dibenzoyl-β-benzildioxime*, m. p. 157—158°, and *dibenzoyl-γ-benzildioxime*, m. p. 135°, are described. Benzoyl-α-benzilmonoxime, m. p. 96°, is obtained from the α-oxime and benzoic anhydride at 60—70°; it is reduced by zinc dust and glacial acetic acid to deoxybenzoin and, in this respect, it resembles the α-oxime. It is therefore regarded as a simple derivative of the latter and not as *ON*-dibenzoyl*iso*benzamide, OBz·CPh:NBz (cf. Werner and Piguet, A., 1905, i, 66; Meisenheimer, *loc. cit.*). Acetyl-α-benzilmonoxime, m. p. 67—68°, can be prepared from the α-monoxime and acetyl chloride in pyridine solution.

The conversion of diacetyl-β-benzildioxime, m. p. 124—125°, when heated above its melting point into a product, m. p. 148°, is accompanied by very slight loss in weight. When hydrolysed by sodium hydroxide, the latter substance gives mainly β-benzildioxime mixed with traces of the anhydride; it is therefore regarded as a dimorphous form of the ordinary diacetyl-β-benzildioxime containing small quantities of diacetyl-γ-benzildioxime.

δ-Benzildioxime (cf. Atack and Whinyates, T., 1921, **119**, 1184) is shown (cf. Brady and Dunn, this vol., i, 292) to be a mixture of much α- with little β-dioxime. H. W.

The Beckmann Transformation. III. J. MEISENHEIMER and H. LANGE (*Ber.*, 1924, **57**, [*B*], 282—289).—A continuation of previous work (Meisenheimer, A., 1922, i, 152).

3 : 5-*Diphenyl*-4-p-*anisyl*isooxazole, $OMe\cdot C_6H_4\leqslant\begin{matrix}CPh\cdot O\\ |\\ CPh{:}N\end{matrix}$, m. p. 189° (cf. Meisenheimer and Weibezahn, A., 1922, i, 176), prepared by the action of boiling sodium hydroxide solution on α-nitro-4-4-methoxystilbene, is converted by ozone in the presence of carbon tetrachloride into *benzoyl*-β-4′-*methoxybenzil*-7-*oxime*,

$$OMe\cdot C_6H_4\cdot CO\cdot C(Ph){:}N\cdot OBz,$$

colourless, prismatic plates, m. p. 95·5—96·5°, the configuration of which is thus established. This compound is also produced by the benzoylation of the 4′-methoxybenzil-7-oxime obtained by Meisenheimer and Jochelson (A., 1907, i, 858) from α-nitro-*p*-methoxystilbene; on hydrolysis, it gives the β-oxime and benzoic acid. The oxime is therefore the β-compound. This conclusion is confirmed by the observation that the oxime is converted by phosphorus pentachloride in the presence of ether into *anisoylformanilide*, $OMe\cdot C_6H_4\cdot CO\cdot CO\cdot NH\cdot Ph$, slender, yellow needles, m. p. 106—107° (the synthesis of which from anisoylformic acid is described). *Acetyl*-β-4′-*methoxybenzil*-7-*oxime*, obtained from the β-oxime and boiling acetic anhydride, forms coarse crystals, m. p. 85—86°.

α-4′-*Methoxybenzil*-7-*oxime*, slender, colourless needles, m. p. 87·5—89°, is prepared by the action of amyl nitrite and sodium ethoxide on *p*-methoxydeoxybenzoin or (better) by treatment of 4′-methoxybenzil-7-oxime-7 : 7′-dimethylacetal,

$$OMe\cdot C_6H_4\cdot C(OMe)_2\cdot CPh{:}N\cdot OH$$

(cf. Meisenheimer and Jochelson, *loc. cit*), with boiling glacial acetic acid. *Acetyl*-α-4′-*methoxybenzil*-7-*oxime*, prepared from the oxime and boiling acetic anhydride, forms coarse, colourless crystals, m. p. 133—134°. *Benzoyl*-α-4′-*methoxybenzil*-7-*oxime*, obtained by benzoylation of the parent substance in the presence of pyridine or from the α-oxime and benzoic anhydride at 40—50°, crystallises in slender, colourless needles, m. p. 137·5—138·5°; it is converted by aqueous-alcoholic sodium hydroxide solution into benzonitrile and benzoic and anisic acids. α-4′-*Methoxybenzil*-7-*oxime methyl ether*, colourless, transparent plates, m. p. 62—63°, is isomerised to the methyl ether of the β-oxime by protracted treatment with hot, concentrated hydrochloric acid.

The view of Meisenheimer and Heim (A., 1907, i, 858) that 4′-methoxybenzil-7-oxime-7′ : 7′-dimethylacetal belongs to the α-series is confirmed by the observations that its methyl ether and *benzoyl* derivative (colourless needles or prisms, m. p. 127—128° dependent on the rate of heating) are converted by glacial acetic acid into the α-oxime or its derivatives, and that the oxime, when dissolved in glacial acetic acid and acetic anhydride, is converted by hydrogen chloride into benzonitrile and anisic acid. H. W.

The Beckmann Transformation. IV. J. MEISENHEIMER and H. MEIS (*Ber.*, 1924, **57**, [*B*], 289—297).—In connexion with

the new conception of the course of the Beckmann transformation (cf. Meisenheimer, A., 1922, i, 152), the behaviour of a number of ortho-substituted benzophenoneoximes has been examined. Although not conclusive in any case, the results generally favour the authors' views. The only case recorded in the literature in which the stereochemical configuration of an oxime is definitely established and harmonises with the older conception of the Beckmann transformation is that of benzoin-α-oxime, which, according to Fischer and Hütz (A., 1895, i, 371), is converted by concentrated sulphuric acid into a derivative of indole, whereas the β-oxime does not behave in this manner. Doubts as to the constitution of the product have been expressed by Fischer (A., 1896, i, 696), but the definite proof that it is not 2-phenylindoxyl is afforded by the synthesis of the latter (Kalb and Bayer, A., 1912, i, 727) and its non-identity with the product obtained by Fischer and Hütz. Loss of water from benzoin-α-oxime must therefore occur in accordance with the scheme:

$$\mathrm{Ph\cdot C(HO\cdot N)\!-\!CH(Ph)\cdot OH} \longrightarrow \mathrm{Ph\cdot C(HO\cdot N)\!-\!CH(C_6H_4)\cdot OH} \longrightarrow \mathrm{Ph\cdot C(HO\cdot N)\!=\!CH(C_6H_4)}$$

which necessitates a transposition of the configurations assigned previously to the α- and β-oximes. The modified conception of the course of the reaction explains the inability of deoxybenzoinoxime or phenylacetaldoxime to give a derivative of indole and the conversion of methylbenzoinoxime and benzoinoxime into the same product. The observation that acetyl-β-benzoinoxime can be oxidised to acetyl-β-benziloxime establishes the relationship between the benzoin- and benzil-oximes, which are thereby brought into complete harmony with one another.

o-Benzoylbenzoic acid is converted by hydroxylamine into an oxime-anhydride, $\mathrm{C_6H_4(CPh{=}N)(CO)>O}$, m. p. 163—164°, which is unaffected by the customary reagents of the Beckmann change but is converted by concentrated sulphuric acid into phthalanil, whereby the oximino oxygen atom changes place with the oppositely situated phenyl radical. *o*-Chloro- and *o*-bromo-benzophenoneoximes lose halogen acid when treated with concentrated sodium hydroxide solution and yield the compound $\mathrm{C_6H_4<\!\!\begin{smallmatrix}CPh\\O\end{smallmatrix}\!\!>N}$, thus rendering the configuration $\mathrm{Br\cdot C_6H_4\cdot C(HO\cdot N)\cdot Ph}$ probable. When treated with ether and phosphorus pentachloride they are converted into *o*-chloro- and *o*-bromo-benzanilide; benzoic *o*-chloro(*o*-bromo)-anilide is not produced, as would be expected from an oxime of the proposed configuration in accordance with the older view of the Beckmann transformation. For analogous reasons, the *syn*-configuration is assigned to the only known form of *o*-hydroxybenzophenoneoxime; it is converted by phosphorus pentachloride into salicylanilide accompanied by small amounts of anhydrobenzoyl-

o-aminophenol, $C_6H_4<\begin{matrix}O\\N\end{matrix}>CPh$, which can be derived only from the stereoisomeric oxime.

o-Aminobenzophenoneoxime exists in two stereoisomeric forms, $NH_2\cdot C_6H_4\cdot \underset{HO\cdot N}{\overset{\|}{C}}Ph$, m. p. 156°, $NH_2\cdot C_6H_4\cdot \underset{N\cdot OH}{\overset{\|}{C}}Ph$, m. p. 126°, the configurations of which are deduced from their behaviour when diazotised. The oxime of higher melting point is transformed by phosphorus pentachloride into the anilide of anthranilic acid, whereas crystalline products are not isolated from the isomeride of lower melting point.

2 : 4-Dimethylbenzophenone-2′-carboxylic acid gives only a single *oxime-anhydride*, $\begin{matrix}CO\cdot C_6H_4\\O\text{——}N\end{matrix}>C\cdot C_6H_3Me_2$, cubic crystals, m. p. 133—134°, which is transformed by concentrated sulphuric acid into 1 : 2 : 4-xylidine and phthalic acid. *Methyl* 2 : 4-*dimethylbenzophenone*-2′-*carboxylate*, coarse, colourless crystals, m. p. 69—70°, b. p. 209—210°/10 mm., could not be caused to react with hydroxylamine.

Mandelanilide is transformed by concentrated sulphuric acid at the ordinary temperature into *phenyloxindole*, $C_6H_4<\begin{matrix}\text{——}N\\CHPh\end{matrix}>C\cdot OH$, colourless, cubic crystals, m. p. 185—187°, but the yields are poor in consequence of simultaneous sulphonation. Mandel-*p*-toluidide, on the other hand, is converted quantitatively into 5-*methyl*-3-*phenyloxindole*, m. p. 211°. H. W.

***p*-Nitrobenzeneazopyrogallol (Chrome Brown P.A.).** P. Juillard (*Mon. Sci.*, 1924, **14**, 25—27).—An account of work already published (A., 1923, i, 1139). E. H. R.

Symmetrical Di*cyclo*hexylhydrazine and Related Compounds. H. H. Harkins and H. L. Lochte (*J. Amer. Chem. Soc.*, 1924, **46**, 450—455).—The authors have investigated the reduction of *cyclo*hexylideneazine by Skita's method. In no experiment did they obtain the unsymmetrical di*cyclo*hexylhydrazine described by Kijner and Beloff (A., 1911, i, 678).

s-*Dicyclohexylhydrazine* (*hydrazocyclohexane*) (*hydrochloride*, white needles, m. p. 271° [corr.]) is very unstable in air, and has m. p. 6—10°; b. p. 260—270°/740 mm.; d_4^{27} 0·9384; n_D^{33} 1·4888. The crystalline *oxalate* and unstable *nitroso* derivative are also described.

Azocyclohexane, $C_6H_{11}\cdot N{:}N\cdot C_6H_{11}$, from di*cyclo*hexylhydrazine by oxidation with bromine water, forms straw-coloured needles, m. p. 34·5°. By hydrolysis of the azo compound with hydrochloric acid, *cyclo*hexylhydrazine (Kijner, *loc. cit.*) is obtained; the thioureide has m. p. 148°, instead of 143° (Kijner); the *benzylidene* compound $(C_6H_{11}\cdot N\cdot N{:}CHPh)_2CHPh$, colourless needles, has m. p. 183° (corr.). cyclo*Hexanone* cyclo*hexylhydrazone peroxide*,

$$C_6H_{11}\cdot NH\cdot N\cdot O\cdot O\cdot C_6H_{10},$$

is formed by the interaction of equivalent amounts of *cyclo*hexyl-

hydrazine and *cyclo*hexanone. It crystallises in fine, white needles, m. p. 76° (decomp.), or when slowly heated, 74°. In contact with air it changes into an oil and a crystalline *substance*, m. p. 136—137°, neither of which has been identified. Attempts to obtain the free *cyclo*hexanone *cyclo*hexylhydrazone in the solid form failed.

Attempts to reduce di*cyclo*hexyl nitrosoamine to as.-di*cyclo*hexylhydrazine by Fischer's method were unsuccessful. A. B. S.

Action of Hydrazine on Hydantoin and Allantoin. R. Fosse, P. Hagène, and R. Dubois (*Compt. rend.*, 1924, **178**, 578—581).—Hydrazine hydrate converts hydantoin, at the ordinary temperature, into hydantoylhydrazide (A., 1923, i, 938). Hydantoylhydrazide affords sparingly soluble crystalline precipitates with aqueous solutions of benzaldehyde and anisaldehyde. *Benzylidenehydantoylhydrazone*, $CHPh:N\cdot NH\cdot CO\cdot CH_2\cdot NH\cdot CO\cdot NH_2$, has m. p. 206—209° (decomp. and varying with rate of heating); p-*methoxybenzylidenehydantoylhydrazone* becomes coloured at 215—220° and melts at 220—227°, the temperatures varying with rate of heating.

Allantoin is converted by hydrazine into the *monohydrate* of *allantoylhydrazide*, $NH_2\cdot NH\cdot CO\cdot CH(NH\cdot CO\cdot NH_2)_2,H_2O$. The anhydrous hydrazide has m. p. 185° (decomp.). Allantoylhydrazide (1 mol.) condenses with xanthhydrol (3 mols.) to give a *substance* (annexed formula), having m. p. 223—225° (decomp.).

$$O<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>CH\cdot NH\cdot NH\cdot CO\cdot CH\left(NH\cdot CO\cdot NH\cdot CH<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>O\right)_2.$$

E. E. T.

Additive Products of the Phosphineimines. M. Masriera (*Anal. Fís. Quím.*, 1924, **22**, 25—48; cf. this vol., i, 234).—A continuation of earlier work on the additive compounds derived from phosphineimines. Acetylphenylchloroamide gives with triphenylphosphine an additive *compound*, probably $Cl\cdot PPh_3\cdot NPhAc$, which is thought to be isomeric with the unstable compound formed from triphenylphosphinephenylimine and acetyl chloride. It is stable in air and forms white tablets having m. p. 109°. Triphenylphosphine and *p*-toluenesulphonephenylchloroamide gives a compound identical with that obtained from toluene-*p*-sulphonyl chloride and triphenylphosphinephenylimine. 2 : 4-*Dichlorophenyl azide* (obtained by the action of sodium nitrite and hydrochloric acid on 2 : 4-*dichlorophenylhydrazine hydrochloride*, white needles, m. p. 205—208° [decomp.]), forms yellow needles, m. p. 51°, and is explosive when dry. With triphenylphosphine in ethereal solution it affords *triphenylphosphine*-2 : 4-*dichlorophenylimine*, $PPh_3:N\cdot C_6H_3Cl_2$, white tablets, m. p. 161°. The last substance is not basic and does not give an additive compound with toluene-*p*-sulphonyl chloride Triphenylphosphine and *p*-toluenesulphone-2 : 4-dichlorophenylchloroamide give an unstable additive *compound*. Various methods for the *N*-chlorination of anilides are studied. G. W. R.

Intensely Coloured Sodium Triphenylboryl, a remarkable Analogue of Sodium Triphenylmethyl. E. Krause (*Ber.*, 1924, **57**, [*B*], 216—217).—A preliminary communication. Ethereal

solutions of boron triphenyl (Krause and Nitsche, A., 1922, i, 694) become intensely coloured in the presence of sodium wire and ultimately deposit orange-yellow, prismatic crystals. The coloured solutions are immediately decolorised by oxygen. H. W.

Organo-chromium Compounds. IV. Chromium Tetraphenyl Hydroxide. F. HEIN and O. SCHWARTZKOPFF (*Ber.*, 1924, **57**, [*B*], 8—14; cf. A., 1921, i, 826; 1922, i, 76, 77).—*Chromium tetraphenyl hydroxide*, $CrPh_4 \cdot OH, 3H_2O$, is prepared by the action of silver oxide on chromium tetraphenyl iodide dissolved in moist chloroform or methyl alcohol, or by the electrolysis of a solution of the iodide in alcohol with a platinum or mercury cathode and rotating silver anode. It crystallises in orange leaflets, m. p. 104—105°, and resembles closely the corresponding pentaphenyl derivative. Measurements of its electrolytic conductivity in aqueous solution show that it is comparable with the alkali hydroxides in strength, whilst comparative experiments in methyl-alcoholic solution show it to be a stronger base than chromium pentaphenyl hydroxide. The base is converted into the corresponding iodide, bromide, and chloride, and into chromium tetraphenylchromitetrathiocyanatodiammine, $Ph_4Cr\left[Cr\begin{matrix}(CNS)_4\\(NH_3)_2\end{matrix}\right]$, which are identical with the compounds obtained previously (with elimination of a phenyl group) from chromium pentaphenyl hydroxide (cf. A., 1922, i, 76). *Chromium tetraphenyl hydrogen carbonate*, $CrPh_4 \cdot HCO_3, 2H_2O$, forms orange crystals, m. p. 110—111°. *Chromium tetraphenyl dianthranilate*, $NH_2 \cdot C_6H_4 \cdot CO_2CrH \cdot Ph_4$, orange needles, m. p. 145—146°, and the *salt*,

$$NH_2 \cdot C_6H_4 \cdot CO_2CrHPh_4, NH_2 \cdot C_6H_4 \cdot CO_2H,$$

m. p. 130°, are also described. H. W.

Structure of Proteins. E. ABDERHALDEN and W. STIX (*Z. physiol. Chem.*, 1923, **132**, 238—250).—With the view of differentiating between dipeptides and the corresponding diketopiperazines the formyl and acetyl derivatives of these compounds have been investigated. *Diformylglycine anhydride* crystallises in rosettes, m. p. 112° (not sharp). A formyl derivative of leucylglycine anhydride could not be prepared. Diacetylglycine anhydride was obtained crystalline (cf. Franchimont and Friedmann, A., 1908, i, 509), also *diacetylglycylalanine anhydride* (m. p. 47°, not sharp) but the *acetyl* derivative of *leucylglycine anhydride* could be obtained only as a syrup. *Diacetyl-leucylglycine* was obtained as a yellow powder (m. p. 95°) by the action of acetyl chloride on the dipeptide. An attempt to prepare bisulphite derivatives of glycine anhydride and silk peptone was unsuccessful. By the reduction of glycine anhydride, alanylglycine anhydride, and leucylglycine anhydride with metallic sodium in ethyl or amyl alcohol, small yields of the corresponding piperazines were obtained. *Dibenzoylmethylpiperazine*, $C_5H_{10}N_2Bz_2$ (crystallising in small plates), and *methylpiperazine dihydrochloride* were prepared from methylpiperazine obtained by reduction of alanylglycine anhydride. The

reduction of diacetylglycine anhydride, diacetylglycylalanine anhydride, and diacetyl-*dl*-leucylglycine anhydride yielded piperazines, whilst from *dl*-leucylglycine and glycyl-*d*-alanine subjected to the same reaction the unchanged compounds were obtained. On applying the method to silk peptone, a mixture of piperazines was obtained yielding crystalline picrates and platinum salts, but these were not further characterised. It is hoped to extend the method to decide whether or not diketopiperazines are present as such in the protein molecule. J. P.

Effect of Ultra-violet Rays on Protein Solutions. R. Mond (*Pflüger's Archiv*, 1923, **200**, 374—378; from *Chem. Zentr.*, 1924, i, 69; cf. A., 1923, i, 868).—Solutions of crystalline egg-albumin or serum-albumin having p_H greater than 4·6 are rendered more acid by ultra-violet radiation, whilst solutions with p_H less than 4·3 are rendered more alkaline. The acidity of suspensions of lecithin is appreciably increased. Sera subjected to radiation have no hæmolytic effect and no effect on an isolated frog's heart. It is supposed that radiation causes the development in sera of substances which exert a dilatory effect on the vascular system. G. W. R.

New Sulphur-containing Amino-acid Isolated from the Hydrolytic Products of Protein. II. Sulphur Excretion after Ingestion. J. H. Mueller (*J. Biol. Chem.*, 1923, **58**, 373—375).—When the amino-acid $C_5H_{11}O_2NS$ (cf. A., 1923, i, 869) is ingested by man, the sulphur which it contains is excreted in the urine in the form of inorganic sulphate. This is further evidence in favour of the view that the compound is a primary cleavage product of proteins. E. S.

Lysolecithins and Lysocephalins. II. Isolation and Properties of Lysolecithins and Lysocephalins. P. A. Levene, I. P. Rolf, and H. S. Simms (*J. Biol. Chem.*, 1924, **58**, 859—871; cf. A., 1923, i, 650).—The mixture of lysocephalin and lysolecithin, resulting from the action of cobra venom on egg yolk, has been separated by fractional crystallisation from chloroform and ether after precipitation with cadmium chloride. Lysocephalin has m. p. 198° (decomp.) and $[\alpha]_D^{35}+2{\cdot}0°$ in glacial acetic acid; lysolecithin, which is much more soluble in solvents, softens at about 100°, decomposes at 263°, and has $[\alpha]_D^{20}-2{\cdot}6°$ in chloroform, and $[\alpha]_D^{35}+0{\cdot}8°$ in glacial acetic acid. Hydrolysis yielded palmitic and stearic acids, whereas lysocephalin only yielded stearic acid. Dissociation constants were found, for lysolecithin $K_1=0{\cdot}18$, $K_2=1{\cdot}3\times10^{-12}$, and the isoelectric range p_H 2·75—9·90; for lysocephalin $K_1=3\times10^{-4}$, $K_2=3{\cdot}4\times10^{-10}$ and isoelectric range p_H 5·5—7·5. The question as to which of these constants is the acid and which the basic one is discussed. The hæmolytic activity of lysolecithin was found to be three times that of lysocephalin. G. M. B.

The Carbohydrate Group of Thymonucleic Acid. H. Steudel and E. Peiser (*Z. physiol. Chem.*, 1924, **132**, 297—300).—Thymonucleic acid on being hydrolysed and steam distilled yields a distillate which gives a red fuchsin-sulphite reaction, a green

coloration with pine shavings, a red coloration with aniline acetate, and with orcinol–hydrochloric acid an intense reddish-violet product soluble in amyl alcohol. The ethereal extract of the hydrolysate gives the same reactions. The reactions formerly regarded as being those of a glucal-like residue are therefore ascribed to a volatile, ether-soluble substance which is regarded as furfuraldehyde. No definite conclusions are drawn as to the nature of the sugar residue responsible for the furfuraldehyde reactions. J. P.

Biochemistry.

Carbon Dioxide Absorption Curve of Human Blood. IV. Relation of the Hæmoglobin Content of Blood to the Form of the Carbon Dioxide Absorption Curve. V. The Construction of the CO_2 Absorption Curve from One Observed Point. VI. The Relationship of the CO_2 of Blood to that of Plasma. J. P. PETERS, H. A. BULGER, and A. J. EISENMAN (*J. Biol. Chem.*, 1924, **58**, 747—768, 769—771, 773—791).—IV. From a number of determinations of the carbon dioxide content of blood and its "true" plasma at various values of P_{CO_2} (*ibid.*, 1923, **55**, 687, 709), the relation of the hæmoglobin content of human blood to the slope of the absorption curve has been studied. The assumption (Van Slyke, Hastings, and Neill, A., 1923, i, 163) that values of individual buffers occurring in a complex system such as blood, when measured by the ratio $\Delta[MHCO_3]/\Delta P_H$ (Van Slyke, A., 1922, i, 893), can be considered as simple additive functions is shown to be unwarranted. Under the restricted conditions of the experiments recorded, the simple difference in the values of blood carbon dioxide content at P_{CO_2} 60 and 30 mm. (written $\Delta[CO_2]_{60-30}$) is a satisfactory and practical measure of buffer. From the scanty data available it seems possible that the buffer values of individual constituents, or at least the two main phases of the blood, when estimated as $\Delta[CO_2]_{60-30}$, may be considered as simple additive functions.

V. The determinants of the slope of the carbon dioxide absorption curve, other than the hæmoglobin concentration, have not yet been completely ascertained, but a method of calculation is now given which allows for this factor. In the relation $\Delta[CO_2]_{60-30}=0{\cdot}334 \times$ (oxygen capacity)$+6{\cdot}3$, cell volume may be substituted for oxygen capacity by means of the further equation: (oxygen capacity)$=0{\cdot}464$ (cell volume) where both are expressed in vols. %. By the use of these relations, together with the graphic logarithmic method previously described (A., 1923, i, 1249), it is possible to construct the absorption curve from any single point. The average deviation of $\Delta[CO_2]_{60-30}$ from the mean in the experiments recorded is 0·5 vol.%

VI. Determinations are recorded of oxygen capacity (h), cell volume, and carbon dioxide content of whole blood $[CO_2]_b$, and of

the carbon dioxide content $[CO_2]_p$ of the plasma at $P_{CO_2}=40$ mm. on a number of specimens of blood, and on others at $P_{CO_2}=30$ and 60 mm. The relation $[CO_2]_p=[CO_2]_b+(0{\cdot}0159[CO_2]_b-0{\cdot}281)h$ is found to hold when $P_{CO_2}=40$ mm. and allows of the calculation of the carbon dioxide content of plasma from that of whole blood. For tensions other than 40 mm., a slightly modified relation is used. G. M. B.

Rates of Reduction and Oxidation of Blood. A. E. KOEHLER (*J. Biol. Chem.*, 1924, **58**, 813—830).—The rate of oxidation and reduction of blood was followed by comparison with fully oxygenated blood in a colorimeter so designed as to allow of rotation of the specimen in a stream of gas. The velocity of the reactions was found to be largely affected by the oxygen tension. An increase of p_H increases the rate of oxidation and depresses the rate of reduction, whilst a decrease of p_H has the opposite effects. The influence of carbon dioxide or lactic acid on the velocities is in accordance with the changes of p_H produced, there being no specific action of carbon dioxide. Certain ions such as $Na^{\cdot}$ modify the oxidation and reduction curves considerably. G. M. B.

Cholesterol and Bicarbonate Content of Blood in Experimental Kidney Diseases. A. STASIEK (*Biochem. Z.*, 1924, **144**, 477—481).—Hypercholesterinæmia can be produced in dogs by inducing kidney disease by such drugs as cantharidine, uranium nitrate, and mercuric chloride. As the animals were fed during the experimental period on diets free from fat and cholesterol it may be assumed that the hypercholesterinæmia is of endogenous origin. Acidosis is not responsible for this metabolic derangement, since the bicarbonate content of the blood remains normal until after the manifestation of the hypercholesterinæmia. It is suggested that this condition is produced, not only because of the damage done to the cells of the kidney by the above agents, but also by the effect of these agents on the lipoids in other parts of the body. S. S. Z.

Amino-acid Content of the Blood in Normal and Pathological Conditions. C. H. GREENE, K. SANDIFORD, and H. ROSS (*J. Biol. Chem.*, 1924, **58**, 845—857).—The amino-nitrogen content of blood as determined by the Folin method (which was found to be trustworthy in presence of an excess of urea) in cases of twenty different pathological conditions was similar to that in the blood of normal persons, namely, between 4·8 and 7·8 mg. per 100 c.c., with an average of 6·3 mg. The level of amino-nitrogen may be increased by flooding the organism with amino-acids during digestion or from the rapid autolysis of body-tissue, but otherwise deviation beyond the limits mentioned is rare. G. M. B.

Effect of Adrenaline on the Composition of Blood under Normal Conditions in Fasting, and in Avitaminosis. D. ALPERN and J. A. COLLAZO (*Z. ges. exp. Med.*, 1923, **35**, 288—295; from *Chem. Zentr.*, 1924, i, 67—68).—Residual nitrogen, urea, sugar, and amino-acids in the blood of fasting dogs were found to be scarcely above normal. Values appreciably above the normal

were obtained with a diet poor in vitamins. The total ethereal extract of blood was depressed in fasting, but increased by a diet low in vitamins. Adrenaline hyperglycæmia was less marked with low-vitamin diet than in fasting. This was the case even with a triple dose of adrenaline. In the case of fasting and normally-fed animals, the administration of adrenaline resulted in a decrease in the total ether extract and the total ethyl alcohol extract of the blood. With a diet poor in vitamins, on the other hand, increases in these values were observed. The adrenaline effect is related to the diminished power of oxidation and assimilation in the body-cells in avitaminosis. G. W. R.

Formation of Methæmoglobin. W. Lipschitz and J. Weber (*Z. physiol. Chem.*, 1924, **132**, 251—274).—The influence of various aromatic and other compounds in converting the blood pigment into methæmoglobin has been investigated. β-Phenylhydroxylamine, hydrazobenzene, and arsenic hydride form methæmoglobin only in the presence of oxygen and have no action on reduced hæmoglobin. Dimethylaminophenyl ether, azo- and azoxy-benzene, and *p*-hydroxyazobenzene are without effect on hæmoglobin. Benzoquinone and its oximes are decreasingly active in forming methæmoglobin in the order given, but quinonechlorimine is five times as active as quinone. Hæmoglobin at 20° brings about a catalytic decomposition of hydroxylamine into nitrogen and ammonia which reaches a maximum when the reactants are present in the proportion 2 mols. of hydroxylamine : 1 mol. of hæmoglobin. Methæmoglobin catalyses the same reaction. Whilst hydroxylamine and α-methylhydroxylamine convert both oxyhæmoglobin and reduced hæmoglobin into methæmoglobin, β-phenylhydroxylamine acts on oxyhæmoglobin only, and when present in excess converts methæmoglobin into reduced hæmoglobin. By treating reduced hæmoglobin with arsenic hydride followed by a little oxygen a, pigment is obtained with a band at 608—625 $\mu\mu$, which on further treatment with oxygen yields methæmoglobin. This is in agreement with the "nitrobenzenehæmoglobin" described by Filehne (*Arch. exper. Path.*, 1878, **9**, 329), and the latter supposed pigment is therefore regarded as unspecific. J. P.

Formation of Porphyrin from Blood Pigment. I. Spectroscopic Properties of Porphyrin Esters. O. Schumm (*Z. physiol. Chem.*, 1924, **132**, 34—61).—By treatment of hæmoglobin free from oxygen, from blood corpuscles, with 25% hydrochloric acid, a porphyrin is formed. The same porphyrin is formed along with hæmatin if fuming hydrochloric acid is used. If, however, the hæmoglobin is treated with 1·3—2·6% of alcoholic hydrogen chloride, in the presence or in the absence of air, no formation of porphyrin occurs. A porphyrin, obtained from hæmatin by treatment with hydrazine hydrate, possesses properties and spectrum similar to those of the porphyrin obtained from hæmoglobin by the action of hydrochloric acid, but it has not been proved that they are identical. The spectroscopic properties of the methyl esters of urinoporphyrin

(Fischer), cotporphyrin, and of Nenki's hæmatoporphyrin are described. W. O. K.

Blood Pigment of *Arenicola*. J. BARCROFT and H. BARCROFT (*Proc. Roy. Soc.*, 1924, **B**, **96**, 28—42).—The blood pigment of *Arenicola* differs from human hæmoglobin in the following facts: (1) the α-absorption bands of the oxy and carboxy compounds are displaced towards the violet end of the spectrum; (2) its affinity for oxygen is much greater, so that gaseous exchange can take place at pressures of oxygen between 2 and 3 mm.; (3) carbon monoxide has only 70 times the affinity for *Arenicola* hæmoglobin that oxygen has (as compared with 250 times for human hæmoglobin). The function of the pigment is probably to act as a reserve store of oxygen for those periods during which the animal has not access to sea-water. C. R. H.

Inorganic Bases and Phosphates in Relation to the Protein of Blood and other Body Fluids in Bright's Disease and in Heart Failure. H. A. SALVESEN and G. C. LINDER (*J. Biol. Chem.*, 1923, **58**, 617—634).—Determinations have been made of the content of certain inorganic constituents (bases and phosphates) and of proteins in the blood plasma of patients suffering from Bright's disease. In the absence of uræmia, the content of calcium and of protein was found to run parallel. In uræmic cases, however, this parallelism was absent, a marked fall in the calcium content occurring with a protein content only slightly below normal; this effect is attributed to a great retention of phosphates in these cases.

From analyses of blood plasma and other body fluids in cases of heart failure, it appears that 55—70% of the serum calcium is diffusible. The non-diffusible calcium is probably bound to proteins. E. S.

Action of Peptone and of Nucleic Acids on the Coagulability of the Blood. J. W. PICKERING and J. A. HEWITT (*Proc. Roy. Soc.*, 1924, **B**, **96**, 77—94).—Intravascular injection of Witte's peptone inhibits coagulation of the blood in tortoises which have been deprived of hepatic activity, and, to a variable extent, in rats and dogs. Addition of peptone to shed blood delays its coagulation if the blood has not been in contact with damaged tissue. Such blood contains fibrinogen, and will clot on dilution with water or on prolonged exposure to air. Similar results are obtained with nucleic acids derived from thymus and yeast. In all cases the anti-coagulant effect is antagonised by the presence of increased amounts of carbon dioxide in the circulating blood; animals can be immunised against the nucleic acid effect by serial intravascular injections of protein-free nucleic acid preparations. C. R. H.

Equilibria involving Calcium, Hydrogen, Carbonate, Bicarbonate, and Phosphate Ions. I. N. KUGELMASS and A. T. SHOHL.—(See ii, 235.)

Physico-chemical Basis of Vital Permeability. IV. R. BRINKMAN and A. VON SZENT-GYÖRGI.—(See ii, 235.)

Relation between Calcium and Protein of Serum in Tetany due to Parathyroidectomy. H. A. SALVESEN and G. C. LINDER (*J. Biol. Chem.*, 1923, **58**, 635—639).—The decrease in serum calcium in parathyroidectomised dogs is not accompanied by a decrease in plasma protein. Apparently, a parallelism between the decrease in calcium and protein (cf. preceding abstract) indicates a decrease in protein-bound calcium and does not lead to tetany, whereas a decrease in calcium without a corresponding decrease in protein (as in parathyroidectomy) indicates, primarily, a decrease in ionised calcium, which leads to tetany. E. S.

Mechanism of Syphilitic Serological Reactions. The Protein Fractions of Human Blood Serum. R. STERN (*Biochem. Z.*, 1924, **144**, 115—137).—A study has been made of the protein fractions of syphilitic and non-syphilitic sera. The so-called euglobulin fraction, comprising a small part of the water-insoluble globulin, has no significance for the typical serological reactions in syphilitic conditions. This is called "Labileglobulin." The separation from sera of a true euglobulin is described and this on peptisation in "Normosal" (Sächsischen Serumwerke) gives positive or negative Wassermann and Sachs-Georgi reactions according to the reaction of the original serum. The residual serum after removal of the euglobulin gives uniformly negative results, whether separated into its fractions or otherwise. The electrical charge of the euglobulin responsible for the specific reactions bears no relation to the positive or negative nature of the tests. Tannin solutions may convert negative into positive sera, and may themselves react positive to the Wassermann and Sachs-Georgi tests. It is tentatively suggested that the specific action of the euglobulin is due to dehydration in accord with the action of tannin in sensitising dyestuff sols. J. P.

Physiology of Digestion. I. The Diastatic Power of the Mixed Saliva of Man, the Horse, Ox, Pig, and Dog, with Observations on the Complex Nature of Salivary Diastase. II. Fluctuations in the Diastatic Power of Mixed Saliva. C. SCHWARZ and K. STEINMETZER (*Fermentforsch.*, 1924, **7**, 229—253).—I. For man the mean diastatic power (D) found was 1600, for the pig only 14. The saliva of the other animals contained no amylase. Amylase exists in the human salivary glands as an inactive proferment which becomes active upon secretion under the influence of the salts (possibly sodium chloride) of the saliva. II. The diastatic power of human saliva becomes constant in the fasting state. R. K. C.

Physiology of Digestion. X. The Effect of Kristallose, Saccharin, and Parasaccharin on Salivary Diastase. C. SCHWARZ and E. BUCHLMAN (*Fermentforsch.*, 1924, **7**, 282—300). **XI. The Effect of Kristallose, Saccharin, and Parasaccharin on Peptic and Tryptic Digestion.** C. SCHWARZ and V. ZELLINGER (*ibid.*, 301—306).—X. These substances have no effect on salivary diastase in concentrations up to 1%. Earlier results

to the contrary are due to failure to control the p_H of the tests. XI. In concentrations such as might be taken by man, these are without effect on protein digestion by pepsin or trypsin. ("Kristallose" is the sodium salt of saccharin.) R. K. C.

Physiology of Digestion. VIII. Digestion in the Crop of the Fowl. C. SCHWARZ and H. TELLER (*Fermentforsch.*, 1924, **7**, 254—269).—The secretion of the crop is a yellow, viscid fluid generally acid to litmus but devoid of amylolytic or proteolytic activity. Lactic acid is generally to be found in the crop contents, but free hydrochloric acid is absent. Food remains many hours in the crop whilst it undergoes swelling (and some autofermentation) preparatory to digestion elsewhere. No absorption of water, salt, or dextrose by the mucous membrane of the crop was detected. R. K. C.

Absorption of Lecithin. F. EICHHOLTZ (*Biochem. Z.*, 1924, **144**, 66—69).—Lecithin (Witte) fed to young dogs produced an increase in the alcohol-ether-soluble organic phosphorus compounds of the blood, but had no effect on the total fat. It is concluded that lecithin is assimilated as such and that its fatty acid residue is not built up into neutral fats. J. P.

Digestion Experiments with the Raw White of Egg. II. The Digestibility of Unbeaten in Comparison with Beaten Whites. M. S. ROSE and G. MACLEOD (*J. Biol. Chem.*, 1923, **58**, 369—371; cf. *ibid.*, 1922, **50**, 83).—In general, the digestion of beaten egg whites is somewhat more complete than that of unbeaten. The average coefficient of digestibility obtained for raw white of egg is 83%, and for cooked white of egg 86%. E. S.

Effect of Reaction Changes upon Human Carbohydrate and Oxygen Metabolism. J. B. S. HALDANE, V. B. WIGGLESWORTH, and C. E. WOODROW (*Proc. Roy. Soc.*, 1924, **B**, **96**, 15—28).—In the alkalosis produced by forced breathing or by ingestion of sodium bicarbonate the preliminary activation of glucose, which is necessary before it can be metabolised, is inhibited, with resulting acetonuria, and hyperglycæmia and glycosuria after less than half the normally tolerated dose of glucose.

The acidosis caused by breathing carbon dioxide has no effect on carbohydrate metabolism; after ingestion of ammonium chloride there is observed a lowering of sugar tolerance in the post-acidotic stage which is probably due to a failure of the glycogenic function of the liver.

Ingestion of sodium hydrogen carbonate causes an increase in the consumption of oxygen, the reverse effect being produced by ammonium chloride. C. R. H.

Clinical Calorimetry. XXXIV. Ketosis and the Respiratory Exchange in Diabetes. H. B. RICHARDSON and W. S. LADD (*J. Biol. Chem.*, 1924, **58**, 931—968).—The fatty acid : glucose ratio, calculated from the data obtained by the calorimetric method previously described (Richardson and Mason, *ibid.*, 1923, **57**, 587),

was found to be parallel to the excretion of acetone compounds. The threshold of ketosis was found at a ratio of about 1·5 to 1, which corresponds with the presence, during oxidation, of 1 mol. of keto-acid for every mol. of glucose. This parallelism is evidence that the respiratory quotient in diabetes is a true measure of oxidation. Diabetic patients were often able to take diets containing a larger proportion of ketogenic substances than is called for by the above-mentioned molecular ratio, which indicates that the proportions of foodstuffs oxidised were not the same as those ingested.

The fall of ketosis observed in diabetic patients, when fasting, is accounted for by the simultaneous drop in the fatty acid : glucose ratio calculated from the calorimetric data. It was due primarily to a decrease in the total metabolism with a consequent diminution in the metabolism of fat and protein.

During fasting there was little or no increase in the total quantity of glucose oxidised when this was computed as being derived from protein and the glycerol of the fat, as well as from the carbohydrate, undergoing metabolism. Fasting reduces the blood-sugar chiefly by depleting the endogenous sources of glucose. There is often an increase in the oxidation of glucose during the subsequent period of restricted diet, but this is not necessarily due to the fast.

G. M. B.

Acetonæmia, especially in Avitaminosis. M. Händel (*Biochem. Z.*, 1924, **144**, 258—264).—Using a micro method based on that of Bang, the acetone content of the blood of normal, starving, phloridzinised, depancreatised, and avitaminosed dogs, and of normal ox and human blood, has been determined. Avitaminosis leads to no increase in the acetone compounds of dog's blood. Normal human blood contains only traces of free acetone, 2 to 4 mg.% as acetoacetic acid, and 3 to 5 mg.% as β-hydroxybutyric acid. Acetonæmia is most marked in depancreatised dogs and in dogs which have been simultaneously starved and phloridzinised. J. P.

Carbohydrate Metabolism. XXI. The Relation of Sugar Excretion to Renal Integrity. F. P. Underhill and G. Wilens (*J. Biol. Chem.*, 1923, **58**, 153—162).—Following experimental tartrate nephritis, the renal threshold for dextrose appears to be alternately raised and lowered. An injection of dextrose increases the hyperglycæmia. E. S.

Physiological Behaviour of Glucosan. J. Kerb. **Glucosan.** J. Kerb and E. Kerb-Etzdorf (*Biochem. Z.*, 1924, **144**, 60—63).—Arising from Grafe's treatment of diabetes with caramel (*Deutsch. Arch. f. klin. Med.*, 1914, **116**, 437) the physiological action of α-glucosan, *l*-glucosan, and lævulosan is under investigation. The administration of α-glucosan to diabetics and to depancreatised dogs does not produce a rise in blood-sugar. In one case of severe diabetes a slight decrease lasting for one hour was observed. J. P.

Some Changes in the Composition of Blood due to the Injection of Insulin. A. P. Briggs, I. Koechig, E. A. Doisy, and C. J. Weber (*J. Biol. Chem.*, 1924, **58**, 721—729).—A series of

analyses of the blood of dogs after injection of insulin, show that the concentrations of glucose, inorganic phosphate, and potassium in the blood are thereby decreased. A parallel increase observed in the concentration of lactic acid present, is believed to be due to the influence of insulin on the reversible reaction : glucose $\rightleftharpoons$ lactic acid. G. M. B.

Insulin and Phloridzin Diabetes. T. P. NASH, jun. (*J. Biol. Chem.*, 1923, **58**, 453—462).—The results reported are of a preliminary nature and appear to indicate that the administration of insulin to a phloridzinised dog does not cause a utilisation of sugar. E. S.

Influence of Insulin on Phloridzin Diabetes. M. RINGER (*J. Biol. Chem.*, 1923, **58**, 483—501).—Injection of insulin into completely phloridzinised dogs causes the oxidation of dextrose. At the same time, deposition of dextrose as glycogen takes place, the protein metabolism and the heat production are reduced, and the excretion of ketonic substances ceases. These results indicate that the effect of phloridzin is due to a transitory injury to the pancreas. It is suggested that, using phloridzinised dogs, insulin might be assayed in terms of the utilisation of dextrose. The maximum utilisation (oxidation) obtained in the present experiments was 0·95 g. of dextrose per unit of insulin. E. S.

Effect of Alcoholic Pancreas Extract (Insulin) on the Behaviour of the Kidneys towards Dextrose. S. VAN CREVELD and E. VAN DAM (*Nederl. Tijdschr. Geneeskunde*, 1923, **67**, II, 1498—1510; from *Chem. Zentr.*, 1924, i, 215).—From experiments on the perfusion of frog kidneys with dextrose solutions after administration of insulin it is concluded that the specific substance of insulin has a direct effect on the kidneys. G. W. R.

What Substance in the Carbohydrate Metabolism is acted on by Insulin? E. TOENNIESSEN (*Z. physiol. Chem.*, 1924, **133**, 158—164).—The author maintains that insulin acts on the lactic acid formed in the metabolism of carbohydrates in the animal organism, since all the previous stages in this metabolic process proceed normally in the absence of the pancreas. He was able to demonstrate that on adding lactic acid to minced pancreas there is no increase in the formation of acetaldehyde, but in the presence of pancreas and minced muscle the amount of acetaldehyde formed was double that formed by the control organs alone. Acetaldehyde was also formed on introducing insulin into normal and more so into diabetic blood. It is supposed to be derived from lactic acid. S. S. Z.

Comparative Study of the Blood-sugar Concentration in the Liver Vein, the Leg Artery, and the Leg Vein during Insulin Action. C. F. CORI, G. T. CORI, and H. L. GOLTZ (*J. Pharm. Exp. Ther.*, 1923, **22**, 355—373).—Determinations of the blood-sugar show that in the rabbit, starved for twenty-four hours, the concentration in the liver vein is on the average 28 mg.% higher than in the neck vein, and 23 mg.% higher than in the

femoral artery, whilst that in the femoral artery is 8 mg.% higher than that in the femoral vein. Under the influence of insulin, the first two figures tend to decrease and the last one to increase, so that there would appear to be diminished output of sugar by the liver, and increased uptake by the muscles. W. O. K.

Physiological Action of Insulin. U. SAMMARTINO and D. LIOTTA (*Arch. Farm. Sperim.*, 1924, **23**, 13—46).—The authors discuss the question of glycæmia in relation to the action of insulin. The blood-sugar content of fasting rabbits following the injection of a unit dose of insulin falls below 0·045 mg.%, and is accompanied by hypoglycæmic convulsions and death. Even after death has been prevented by intravenous injection of dextrose (1 g. per kg. body weight), hypoglycæmia persists for 3—5 days. After repeated unit doses, recovery through injection of sugar is no longer possible. Administration of sucrose, or of dextrose in amount less than 1 g. per kg. body weight, does not prevent death from hypoglycæmia. Insulin also produces a fall in glycæmia in hyperglycæmia produced by adrenaline or lesion of the fourth ventricle. Hypoglycæmic coma and death are not prevented by administration of vaso-constrictive substances, such as ergotine and pituitary extract. Injection of insulin produces a lowering of blood pressure which cannot be neutralised by intravenous injection of sugar. G. W. R.

Glucokinin. III. An Apparent Synthesis in the Normal Animal of a Hypoglycæmia-producing Principle. Animal Passage of the Principle. J. B. COLLIP (*J. Biol. Chem.*, 1923, **58**, 163—208).—The marked hypoglycæmia and other symptoms which are produced in normal rabbits by the injection of glucokinin (A., 1923, i, 1247) have also been observed after injection of guanidine sulphate or of overdoses of insulin, and after prolonged fasting; hypoglycæmia also occasionally occurs spontaneously, in which case *Coccidia oviforme* have been found in the liver. Transitory relief of the symptoms may be effected by injection of dextrose, but the death of the animal ultimately results. When defibrinated blood or serum from such hypoglycæmic rabbits is injected into normal rabbits, similar symptoms occur, animal passage (rabbit) of the hypoglycæmia-producing principle apparently being capable of indefinite extension. The principle is thermostable, undergoes dialysis, and is precipitated from blood by ammonium sulphate, but not by tungstic acid. E. S.

Aqueous Extracts of Pancreas. II. Physical and Chemical Behaviour of Insulin. H. A. PIPER, R. S. ALLEN, and J. R. MURLIN (*J. Biol. Chem.*, 1923, **58**, 321—336).—Observations which have been made during the preparation of insulin lead to the conclusion that insulin is not a protein; it appears, however, to exist in the pancreas in combination with protein. The purest preparations of insulin are fairly stable and may be stored for 4 months without loss of potency; solutions may be heated at 80° for half an hour without marked destruction. Insulin

does not diffuse readily through parchment membranes; it is adsorbed by charcoal from acid but not from neutral solution.

E. S.

Aqueous Extracts of Pancreas. III. Some Precipitation Reactions of Insulin. C. P. KIMBALL and J. R. MURLIN (*J. Biol. Chem.*, 1923, **58**, 337—346).—In developing a method for the preparation of insulin from aqueous extracts of pancreas a large number of both organic and inorganic precipitants have been tested, but the majority have been rejected owing to the difficulty of removing them from the precipitate. Among the more successful precipitants are amyl alcohol and sodium chloride. The former is used in conjunction with ethyl alcohol. Four to five volumes of ethyl alcohol are added to the aqueous extract; the addition of amyl alcohol then causes the insulin to separate as a solid layer between the aqueous and the alcoholic layers. Acetone also precipitates the insulin but it has the disadvantage that it precipitates at the same time a substance, to which the name *glucagon* is given, which produces a distinct hyperglycæmic effect in animals; it may be removed from the precipitated insulin by extraction with 95% alcohol. Saturation of an aqueous extract with sodium chloride causes complete precipitation of the insulin. Sodium chloride has the advantage over ammonium sulphate that traces of it are not harmful to the organism, whereas the ammonium sulphate, if not completely removed from the precipitate, may cause a hyperglycæmic reaction.

E. S.

Action of Ammonium Hydroxide and other Alkaline Compounds on Insulin. E. J. WITZEMANN and L. LIVSHIS (*J. Biol. Chem.*, 1923, **58**, 463—474).—Treatment of insulin with 0·5 or 0·7*N*-ammonia or with 0·1*N*-sodium or potassium hydroxide for some days causes complete inactivation. When ammonia has been employed, the activity may be quickly restored by acidification with hydrochloric acid; inactivation by sodium or potassium hydroxide, however, is irreversible. Sodium carbonate and hydrogen carbonate and disodium hydrogen phosphate have scarcely any action on the activity of insulin. When insulin is treated with mixed alkalis the inactivation may be either accelerated or retarded according to the mixture employed. The effect of ammonia is regarded as indicating a tautomeric change in the molecule.

E. S.

Chemical Reactions of the Substance containing Insulin. H. A. SHONLE and J. H. WALDO (*J. Biol. Chem.*, 1924, **58**, 731—736).—A detailed chemical examination of an insulin preparation from the pancreas of hogs. Precipitation and other methods of purification failed to separate a physiologically active substance of constant ultimate composition. The preparation appeared to be a complex mixture of proteoses, and the active principle itself may either be a proteose or be intimately associated with a proteose fraction.

G. M. B.

Adrenaline Secretion in Adrenaline Glycæmia. P. TRENDELENBURG (*Pflüger's Archiv*, 1923, **201**, 39—55; from *Chem. Zentr.*, 1924, i, 212).—Decomposition of glycogen results from the administration of smaller amounts of adrenaline than has been previously supposed. Blood-sugar in rabbits was increased by continuous administration of 0·00006—0·0001 mg. of adrenaline per kg. live weight per minute. Glycosuria does not appear unless larger doses are given. The secretion of adrenaline by the suprarenal bodies after the production of adrenaline hyperglycæmia was found to be more than 0·0005 mg. per kg. live weight per minute, a rate of production sufficient to cause glycosuria within a short time. There is probably a direct nervous stimulation of the liver cells in addition to the chemical effect. G. W. R.

Carbohydrate Metabolism of *Ascaris Megalocephala*. A. FISCHER (*Biochem. Z.*, 1924, **144**, 224—228).—In view of the fact that the acid formation in autolysis of *Ascaris megalocephala* is accounted for by the breakdown of glycogen to lactic acid and carbon dioxide, doubt is expressed regarding the conclusions of Weinland (*Z. Biol.*, **42**, **43**), who regarded the acidity as being due to valeric acid, and the carbohydrate metabolism of these worms as being abnormal. J. P.

Fat Metabolism in Avitaminosis. V. Distribution of Fats and Lipoids in the Liver after Phosphorus Poisoning in Normal, Starving, and Avitaminosed Animals. K. ASADA (*Biochem. Z.*, 1924, **144**, 203—211).—A histological study of the distribution of neutral fat in the livers of normal, starved, and avitaminosed rats confirms the author's earlier observations (A., 1924, i, 122, 245), but as regards lipoids, the microscopical appearance of the phosphorus-poisoned avitaminosed liver is the same as that of the poisoned normal liver despite the increased cholesterol content of the former as revealed by chemical methods. The conclusions of Salvioli and Sacchetto (*Frankf. Z. Path.*, 1922, **28**) regarding the effect of phosphorus poisoning on the fat and lipoid content of the livers of normal and starving dogs are based on too short periods of starvation. J. P.

Comparative Metabolism of certain Aromatic Acids. V. Fate of some Ring Substitution Products of Phenylacetic Acid in the Organisms of the Dog, Rabbit, and Man. L. R. CERECEDO and C. P. SHERWIN (*J. Biol. Chem.*, 1923, **58**, 215—224).—When fed to human beings, dogs, or rabbits, *o*-nitrophenylacetic acid, *o*-aminophenylacetic acid, *o*-hydroxyphenylacetic acid, *o*-chlorophenylacetic acid, and 2 : 4-dinitrophenylacetic acid were excreted unchanged with the following exceptions: *o*-aminophenylacetic acid, which was excreted by rabbits in an acetylated form, and *o*-chlorophenylacetic acid, which was conjugated with glycine both in man and in the dog and excreted as *o*-chlorophenaceturic acid. All the above acids were less toxic than phenylacetic acid. The results show that *o*-compounds are not readily oxidised in the organism and that they are not necessarily more toxic than the *m*- and *p*-isomerides.

o-*Chlorophenaceturic acid*, m. p. 135°, has been synthesised from glycine and o-*chlorophenylacetyl chloride*, b. p. 119—121°/12 mm. The latter substance was obtained by the action of phosphorus pentachloride on *o*-chlorophenylacetic acid. E. S.

Detection of Pyruvic Acid in Muscle and Liver. L. J. Simon and E. Aubel (*Compt. rend.*, 1924, **178**, 657—659; cf. A., 1923, i, 875).—Pyruvic acid is not destroyed under aseptic conditions by macerated liver or fresh muscle. If injected as the sodium salt *in vivo* into the liver, it disappears, but not rapidly. Alanine, dextrose, and sodium lactate under similar conditions are not converted into detectable quantities of pyruvic acid. The latter, however, may possibly be produced in very small quantities, or undergo immediate conversion into other substances. E. E. T.

Specific Dynamic Action of Proteins. P. Liebesny (*Biochem. Z.*, 1924, **144**, 308—350).—The specific dynamic action of proteins, following the ingestion of 200 g. of flesh and 100 g. of bread, reveals itself in an increase of 20—40% above the oxygen consumption shown in the resting and fasting condition, the maximum increase occurring in from 1 to 2½ hours after the meal. For any one individual, the specific dynamic action is constant under like conditions over a period of some months. It is diminished or entirely lacking in cases of affection of the hypophysis and in conditions involving disturbance of the autonomic nervous system. Administration of preparations of the anterior lobe of the pituitary gland produces an increase in the specific dynamic action. J. P.

Adsorption of Amino-acids by Animal Tissues. W. Moeller (*Biochem. Z.*, 1924, **144**, 152—158).—Hide powder adsorbs tyrosine from aqueous solution to the extent of 45% in 10 days. Importance is attached to the part played by such adsorption phenomena in the biosynthesis and hydrolysis of proteins. J. P.

Arginine Metabolism. K. Felix and K. Morinaka (*Z physiol. Chem.*, 1924, **132**, 152—166).—*dl*-Arginine, when passed through the liver of a cat, is hydrolysed fairly completely into ornithine and urea, both isomerides being attacked. Arginine, absorbed through the intestinal wall and then allowed to pass through the liver, is similarly hydrolysed by the liver. On the other hand, arginine in clupeon, which is built up of 2 mols. of arginine and 1 mol. of a monoamino-acid, is not hydrolysed by the liver. It would appear, therefore, that arginine, after absorption from the intestine, escapes complete destruction by the liver by being at least partly combined in the form of a polypeptide. W. O. K.

Animal Calorimetry. XXIII. Influence of the Metabolism of the Nucleic Acids on Heat Production. M. Ringer and D. Rapport (*J. Biol. Chem.*, 1923, **58**, 475—482).—It is concluded from experiments on dogs that nucleic acids exert no specific dynamic effect. E. S.

Metabolism of *l*-Pyrrolidonecarboxylic Acid and its Stability to Acids and Alkalis. R. M. Bethke and H. Steenbock (*J. Biol. Chem.*, 1923, **58**, 105—115).—When fed in large amounts to pigs maintained on a starch diet, pyrrolidonecarboxylic acid is partly metabolised and partly excreted unchanged. No increase occurs in the amino-nitrogen content of the urine, thus indicating that the hydrolysis of the acid is not sufficiently rapid to lead to the production of glutamic acid in amounts greater than those which the organism can deaminise. The acidity and alkalinity of the alimentary canal are insufficient to account for the hydrolysis. E. S.

Effects of Iodides on Nitrogen Metabolism. G. P. Grabfield, B. J. Alpers, and A. M. Prentiss (*J. Pharm. Exp. Ther.*, 1924, **22**, 393—400).—Administration of sodium or potassium iodides to man increases the output of nitrogen in the urine; the latter salt also increases the non-protein nitrogen of the blood. W. O. K.

Effect of Reaction Changes on Human Inorganic Metabolism. J. B. S. Haldane, V. B. Wigglesworth, and C. E. Woodrow (*Proc. Roy. Soc.*, 1924, **B**, **96**, 1—14).—The alkalosis of forced breathing produces a fall in the inorganic phosphate of the blood accompanied by a fall in the excretion in the urine; the reverse effects are observed in the acidosis caused by the breathing of carbon dioxide. The ingestion of sodium bicarbonate produces no effect. In the acidosis following ingestion of ammonium chloride there is a heavy excretion of phosphate in the urine which falls off with the exhaustion of the available store of phosphate in the body, the immediate cause of the falling off being the low concentration of phosphate in the blood. Ammonium chloride acidosis also causes the body to lose large amounts of water, sodium, and potassium. C. R. H.

Acid–Base Metabolism. I. Determination of Base Balance. A. T. Shohl and A. Sato (*J. Biol. Chem.*, 1923, **58**, 235—255).—Analyses have been made of the food, urine, and fæces of four male infants less than 1 year old. For purposes of calculating the acid–base balance, only sodium, potassium, calcium, magnesium, sulphates, phosphates, and chlorides are considered. Sulphur and phosphorus contained in the food are regarded as acidic constituents to the extent that they are oxidised in the organism to sulphates and phosphates. The results show that there is a normal positive base balance equivalent to 10 c.c. $\pm$2 c.c. of 0·1*N* base per kg. per day. This balance is lowered by the addition of hydrochloric acid to the diet and raised by the addition of sodium hydrogen carbonate. The acid added to the food is excreted in the urine; the base, however, is excreted partly in the urine and partly in the fæces. E. S.

Acid–Base Metabolism. II. Mineral Metabolism. A. T. Shohl and A. Sato (*J. Biol. Chem.*, 1923, **58**, 257—266).—Hydrochloric acid increases the excretion of ash, nitrogen, calcium, sodium, phosphorus, and chlorine in the urine of infants, and of ash,

nitrogen, calcium, magnesium, and chlorine in the fæces, and decreases that of phosphorus in the fæces; the excretion of potassium, magnesium, and sulphur in the urine and of sodium and potassium in the fæces is unaffected. The net result is a decreased retention of ash, nitrogen, calcium, magnesium, sodium, potassium, phosphorus, sulphur, and chlorine. Sodium hydrogen carbonate increases the excretion of ash, nitrogen, sodium, potassium, sulphur, and chlorine in the urine, and of ash, nitrogen, calcium, sodium, potassium, phosphorus, sulphur, and chlorine in the fæces; it decreases the calcium, magnesium, and phosphorus in the urine, and the magnesium in the fæces. In this case, the net result is an increased retention of magnesium and sodium and a decreased retention of ash, nitrogen, calcium, potassium, phosphorus, sulphur, and chlorine. E. S.

Calcium Content of the Organs of Cats Treated with Calcium [Salts]. III and IV. H. JUNGMANN and M. SAMTER (*Biochem. Z.*, 1924, **144**, 265—269).—III. Determinations have been made of the distribution of calcium in the tissues of cats to which intravenous injections of calcium chloride and of calcium fructosephosphate had been given. After chloride administration the kidney showed a very high calcium content, and the lesser intestine, in contrast to that of normal animals, showed a uniform distribution of calcium along its entire length. Injection of calcium fructosephosphate, which has a more marked effect than has the chloride in increasing the calcium of the tissues generally, gave a notable increase in the calcium content of liver and kidney. IV. Intravenous injection of calcium chloride produces a greater increase in the calcium of the cat's kidney than does subcutaneous administration (cf. Heubner and Rona, A., 1923, i, 415). After intravenous injection of calcium fructosephosphate, the blood-serum and liver contain up to six times as much calcium as does the blood or liver of normal cats, or of cats given subcutaneous injections of calcium chloride. In acute calcium poisoning the calcium content of the skin may possibly be increased. Repeated injection of calcium acetate produces no alteration in the calcium content of the liver, heart, or other organs, nor does it affect the growth curves of the cats, as does subcutaneously administered calcium chloride (cf. Heubner and Rona, *loc. cit.*). J. P.

Metabolism of Inorganic Salts. IV. The Content of Inorganic Salts in the Blood in Pregnancy, with Especial Reference to Calcium. F. P. UNDERHILL and ALICE DIMICK (*J. Biol. Chem.*, 1923, **58**, 133—140).—In general, little change occurs in the inorganic constituents of the blood during pregnancy, although the calcium content (determined on whole blood) is somewhat higher for pregnant than for non-pregnant women. The calcium content does not vary in a regular manner with the course of pregnancy. These results give no support to the view that an increased calcium content of the blood is of significance in the induction of labour. E. S.

Metabolism of Inorganic Salts. V. Inorganic Salt Metabolism in Cocaine Poisoning. F. P. UNDERHILL and E. G. GROSS (*J. Biol. Chem.*, 1923, **58**, 141—146).—No change is produced in the inorganic constituents of the blood by cocaine poisoning. The relief afforded by the administration of calcium salts is due to their action as central nervous depressants. E. S.

Absorption of Metallic Salts by Fish in their Natural Habitat. II. The Absorption of Nickel by *Fundulus Heteroclitus*. A. THOMAS (*J. Biol. Chem.*, 1924, **58**, 671—674; cf. *ibid.*, 1912, **11**, 381).—Nickel salts are not toxic to the *Funduli* in sea-water, but are extremely so in fresh-water, death being preceded by signs of intoxication in the fish. A number of analyses are given showing the dependence of the nickel absorbed on the concentration of the solution and on the time of immersion.

G. M. B.

Method of Determining the Biological Value of Protein. H. H. MITCHELL (*J. Biol. Chem.*, 1924, **58**, 873—903).—Details of the experimental methods are given, by which trustworthy data are secured on the nitrogenous metabolism of rats. The "metabolic nitrogen" of the fæces is measured by the total excretion of fæcal nitrogen on a nitrogen-free diet adjusted to have a "roughage" content approximately equal to that of the normal protein-containing diet. The excretion of nitrogen in the urine resulting from the catabolism of the tissues is not markedly depressed by protein feeding. The true basal catabolism of nitrogenous substances in the tissues is therefore measured by the total excretion of nitrogen in the urine in an adjacent period of feeding a nitrogen-free diet. This basal value is, however, subject to unexplained variations and must be redetermined at intervals in any long series of experiments.

The biological value of a protein is given by the percentage of the absorbed nitrogen (nitrogen intake — fæcal nitrogen of dietary origin) that is not eliminated in the urine. This value for the protein of a food is practically a coefficient of digestibility applied to the total protein present, and by means of it a "net protein value" of the food may be calculated. G. M. B.

Biological Value of Proteins at Different Levels of Intake. H. H. MITCHELL (*J. Biol. Chem.*, 1924, **58**, 905—922).—The biological values of the proteins (total nitrogen) of milk, maize, oats, rice, yeast, potatoes, navy beans, and the packing house by-product "tankage," have been determined by a modified Thomas method (preceding abstract). In the case of maize, milk, oats, and potatoes, experiments were made with rations containing 5 and 10% of protein, and, except for potatoes, the biological values were smaller at the higher level; the reasons for this are discussed. G. M. B.

Supplementary Relations among Proteins. H. H. MITCHELL (*J. Biol. Chem.*, 1924, **58**, 923—929).—If the biological value of the proteins in a mixture of two foods is found to be higher than that

calculated from the values for each food used separately, assuming the effect to be directly additive, this shows the existence of a supplementary relation between the proteins of the two foods in question. A considerable supplementary relation has been shown to exist between the proteins of maize and of milk, and between those of maize and of "tankage." No such relation could be detected between gelatin and the proteins of the oat kernel. G. M. B.

Vitamins. I. Antineuritic Vitamins. G. GAGLIO (*Atti R. Accad. Lincei*, 1923, [v], **32**, ii, 479—482).—Many different substances are able to exert antineuritic properties, some of them removing all, and others only certain, of the symptoms of experimental polyneuritis in pigeons. Of all the materials which have been investigated, rabbits' urine produces the most complete and permanent antineuritic effects. Investigations are necessary to ascertain the action of different mixtures of the chemical compounds known to occur in urine or blood plasma when administered to pigeons in conjunction with polished rice. The known facts warrant the statement that the conception of a single specific antineuritic principle is not justifiable. T. H. P.

Presence of Vitamin-*A* in Commercial Lecithin. F. EICHHOLTZ (*Biochem. Z.*, 1924, **144**, 70—71).—From feeding experiments on white mice the presence of vitamin-*A* in lecithin (Witte) is inferred. J. P.

Effect of Diet on the Content of Vitamin-*B* in the Liver. T. B. OSBORNE and L. B. MENDEL (*J. Biol. Chem.*, 1923, **58**, 363—367).—When rats are maintained on a diet free from vitamin-*B*, the normal store of this factor in the liver is to a large extent depleted. E. S.

Fat-soluble Vitamins. XV. Calcium and Phosphorus Relations to Growth and Composition of Blood and Bone with Varying Vitamin Intake. R. M. BETHKE, H. STEENBOCK, and M. T. NELSON (*J. Biol. Chem.*, 1923, **58**, 71—103).—Normal calcification takes place in the bones of rats maintained on a diet otherwise deficient in fat-soluble vitamins when 20 c.c. of skimmed milk or 1 c.c. of whole milk per rat per day is added to the diet; with smaller additions, the calcification is poor.

The femurs and humeri of normal rats yield 45% of ash at the age of 24 days, 59% at 66 days, and 66% at maturity. The blood phosphates and calcium are slightly higher in young than in old animals.

A quantitative relation appears to exist between vitamin and calcium whereby poor assimilation of the latter due to deficiency of the former in the diet may be counteracted by increases in the calcium content of the diet. When, owing to lack of vitamin or of calcium salts, normal growth does not occur, there is a tendency for the calcium content of the blood and the ash content of the bones to suffer a diminution. Absence of fat-soluble vitamins from the diet depresses the calcium content of the blood, the depression being

increased by the addition of phosphates to the diet; radiation with ultra-violet light for 10 minutes per day increases both the calcium and phosphorus content of the blood. E. S.

Influence of Diet on Teeth and Bones. G. Toverud (*J. Biol. Chem.*, 1923, **58**, 583—600).—When guinea pigs are maintained on a diet deficient in antiscorbutic vitamin, both histological and chemical changes occur in the front teeth. The total ash and calcium content decrease whilst the magnesium content increases. White rats fed on a diet poor in calcium show a low calcium and a high magnesium retention and fail to breed normally. Their bones are low in total ash, calcium, and phosphorus, whilst the composition of their teeth is abnormal, the molars being low in total ash, slightly low in calcium and phosphorus, and slightly high in magnesium, and the front teeth low in all respects. Changes in the diet can thus produce chemical changes in a formed tooth. E. S.

Effect of Hæmatoporphyrin on the Deposition of Calcium in the Bones of Rachitic Rats. E. C. van Leersum (*J. Biol. Chem.*, 1924, **58**, 831—844).—Injection of hæmatoporphyrin causes a great increase in sensitiveness of the subject to rays of light lying within the visible part of the spectrum. The effect of such injections was therefore studied on rats in which, by a restricted diet, signs of rickets had been produced. *X*-Ray- and photomicrographs are given showing that under this treatment deposition of calcium was proceeding and the effects were similar to those of cod-liver oil or irradiation treatment. Direct proof of the influence of light has not yet been obtained. G. M. B.

Dietary Requirements for Reproduction. I. Nutritive Value of Milk Proteins from the Point of View of Reproduction. II. Existence of a Specific Vitamin for Reproduction. B. Sure (*J. Biol. Chem.*, 1924, **58**, 681—692, 693—709).—Rats fed on a complete artificial diet, with milk protein as a source of nitrogen, were found either to be sterile or to be unable to rear their young. Cod-liver oil was substituted for butter fat as a source of vitamin-*A*; vitamin-*B*, the antirachitic factor, and the necessary salts and iodine were provided. The further addition of casein, arachin, or edestin with 0·4% of cystine and in other experiments of lysine, proline, tyrosine, and trytophane still failed to secure normal reproduction.

From these experiments and those of Evans and Bishop (*J. Metabol. Research*, 1922, **1**, 319, 335; 1923, **3**, 201, 233) it is concluded that there exists another hitherto unrecognised vitamin which is essential for reproduction. This factor has been found by breeding experiments to be present in Georgia velvet bean pod meal, polished rice, yellow corn, and rolled oats.

Accepting Macdonald's opinion that the "vitamin-*D*" of Funk and Dubin (A., 1922, i, 203) is wrongly classified as a vitamin, the term "*D*" is proposed for the antirachitic factor of McCollum and others (*J. Biol. Chem.*, 1922, **53**, 293), and the term "*E*" is adopted for the new vitamin which affects reproduction. G. M. B.

Chemical Changes in the Lipoids of Kidneys with Degenerated Cells. P. SCHNAPP (*Z. physiol. Chem.*, 1924, **133**, 62—79).—By clamping the vascular system of the kidney degeneration is induced in the cells of this organ. The ethereal extract of such degenerated kidneys showed a lower total lipoid content, a lower acidity (Spaltungzahl), and a lower iodine value than the normal kidney. On the other hand, the unsaponifiable and the saponifiable (Restzahl) residue showed an increase above the normal. S. S. Z.

R. Engeland and W. Biehler's Article "Some Compounds Extracted from Human Skeletal Muscle" (A., 1923, i, 72). J. A. SMORODINCEV (*Z. physiol. Chem.*, 1924, **132**, 328).—Attention is directed to the investigations by the author on the extractives of human and mammalian skeletal muscle (*Z. physiol. Chem.*, 1913, **87**, 12; 1914, **92**, 214; 1922, **123**, 116). J. P.

Saccharophosphatase in Human Organs. E. FORBAI (*Biochem. Z.*, 1924, **144**, 149—151; cf. A., 1922, i, 960; 1924, i, 120).—Saccharophosphatase is present in normal human pancreas and suprarenal bodies, but is absent from normal kidneys, testes, heart muscle, thyroids, skeletal muscle, and blood-serum. In cancerous conditions, it is found in certain organs (notably the liver) from which it is normally absent. J. P.

State of Combination of Nucleic Acids in Cell Nuclei. H. STEUDEL and T. TAKAHATA (*Z. physiol. Chem.*, 1924, **133**, 165—172).—The nucleic acid of yeast-cells is present in a free state and not in combination with protein. Nucleic acid was obtained from yeast by extraction with sodium chloride and precipitation with hydrochloric acid by Clarke and Schryver's method. S. S. Z.

Biological Significance of Nucleic Acid Compounds. E. HAMMARSTEN (*Biochem. Z.*, 1924, **144**, 383–465).—An important paper, in which the conductivity, hydrogen-ion concentration, osmotic pressure, and viscosity of thymus nucleic acid and its salts have been studied and discussed.

Thymonucleic acid is a strong polyphosphoric acid in which each of the four phosphorus atoms is associated with one dissociable hydrogen atom. Fresh thymonucleic acid dissolves to a concentration of about $3 \times 10^{-3}M$, yielding a turbid solution. It is supposed that the suspended particles causing the turbidity are due to the undissociated acid. From dialysis experiments carried out on the quadrivalent sodium salt of thymonucleic acid it is found that the salt possesses an apparent degree of dissociation of 0·25. The sodium salt of thymonucleic acid shows an osmotic pressure corresponding with that of the undissociated salt. On the other hand, when the acid is in combination with trimethyl-, triethyl-, or tripropyl-amine or with tetramethylammonium hydroxide, the osmotic pressure increases with the increase in volume of the cation. The sodium salt manifests the Donnan equilibrium in neutral solution. The relative viscosity of the sodium salt is very high, and it combines in dilute solutions with about 400 times its volume of water. Various agencies which lower the viscosity of its solution bring about an only

partly reversible gel formation, which is most probably due to a phase reversal. The relative viscosity of the sodium salt is reduced by kations even in concentrations of less than $10^{-3}N$. The valency of the kations is of importance. Strong acids reduce the relative viscosity of sodium thymonucleate; the maximum reduction is reached when two of the sodium atoms are replaced by hydrogen. The viscosity of protein–nucleic acid salts is raised by the addition of sodium chloride, probably because of the formation of the tetrasodium salt by double decomposition. The ampholyte salts of thymonucleic acid are hydrolysed during dialysis if the ampholyte is diffusible. Salts of thymonucleic acid and proteins with an isoelectric point of p_H 4·7 exist as precipitates in equilibrium with the protein in hydrogen-ion concentrations approximating to the isoelectric point. When an excess of the sodium salt of thymonucleic acid is added, the protein salts dissolve in water at lower hydrogen-ion concentrations than $3-3{\cdot}5\times10^{-3}$. Protein and thymonucleic acid combine in varying proportions. Proteins with an isoelectric point of p_H 4·7 combine with thymonucleic acid during the first two stages of dissociation of the acid more readily than during the later stages of dissociation. Double decomposition takes place when the neutral salts of thymonucleic acid and diamino-acids are dialysed in the presence even of small quantities of sodium chloride with the formation of the sodium salt of the nucleic acid and the chloride of the diamino-acid. Histone compounds of thymonucleic acid are soluble in water when at least two of the sodium atoms of the salt and an equivalent of histone are in combination with 1 mol. of nucleic acid. The bearing of the above experimental observations on the biology of the cell is fully discussed, particularly with regard to the importance of the Donnan effect. S. S. Z.

Carbohydrate Group of Thymonucleic Acid. H. Steudel and E. Peiser.—(See i, 438.)

Distribution of Pentose Compounds in the Pancreatic Tissues of the Ling Cod (*Ophiodon Elongatus*, Girard). C. Berkeley (*J. Biol. Chem.*, 1923, **58**, 611—616).—Considerably more pentose is present in the islet than in the zymogenous tissue of the pancreas of the ling cod. It is suggested that it is produced from dextrose which has been activated by insulin.

E. S.

Nitrogenous Extractives from the Spleen. S. Demianowski (*Z. physiol. Chem.*, 1924, **132**, 109—133).—In spite of careful investigation of the phosphotungstic acid precipitate from the extract of the spleen of the freshly-killed ox, the presence of carnitine, methylguanidine, or of carnosine could not be detected. Tryptophan, approximately 0·0056% of the fresh horse spleen pulp, is extracted by water at 55—60°. Tryptophan is also extracted under similar conditions from the fresh spleens of oxen. Organic compounds other than tryptophan such as arginine, carnosine, tyrosine, or cystine are precipitated by Hopkins' reagent.

W. O. K.

Hydrogen-ion Concentrations within the Alimentary Tract of Insects. W. J. CROZIER (*J. Gen. Physiol.*, 1924, **6**, 289—293).—Larvæ of dipterous insects (*Psychoda* and *Chironomus*) were kept in solutions containing an indicator (bromophenol blue, phenol red, or neutral red), and then removed and dissected. The colours of the fluid in the various sections of the intestinal canal indicated that the p_H was approximately as follows: in the œsophagus, 7·1; the cardiac chamber, 6·2; the mesenteron, 7·5; and the hind-gut, 6·4. W. O. K.

Behaviour of Calcium, Potassium, Chlorine, and Phosphorus in Milk and the Technique of Ultrafiltration. C. WHA (*Biochem. Z.*, 1924, **144**, 278—284).—Fifty % of the calcium of cow's milk is present in a colloidal non-diffusible form (cf. Rona and Michaelis, *ibid.*, 1909, **21**, 114), but in the process of souring all the calcium becomes ionised and diffusible. Of the phosphorus in milk 60% is in a colloidal state, whilst all the potassium and chlorine present is diffusible (cf. György, this vol., i, 120). A vacuum dialyser of collodion is described. J. P.

Influence of Phosphate and Bicarbonate on the Dissociation of Calcium Compounds in the Cerebro-spinal Fluid. H. BEHRENDT (*Biochem. Z.*, 1924, **144**, 72—80).—Using the method of Brinkman and van Dam, 20% of the total calcium (5 mg.%) of the cerebro-spinal fluid of children is found in the ionised condition at p_H 7·6—7·7. Sodium hydrogen carbonate and sodium hydrogen phosphate solutions of the same p_H as the fluid markedly lower the calcium-ion concentration, the phosphate exerting an effect more than twice that of the carbonate. J. P.

Ferments in the Amniotic Fluid. K. MAEDA (*Biochem. Z.*, 1924, **144**, 1—8).—The reaction of the amniotic fluid varies between p_H 7·5 and 7·7. Diastase is present in the fluid in greater amount than in the blood from which it is derived. Lipase is sometimes present and originates from the fœtal intestine. Pepsin, rennin, and thrombin (fibrin ferment) occur only in traces. Trypsin is absent. J. P.

Urinary Excretion of Organic Acid and its Variation with Diet. L. MCLAUGHLIN and K. BLUNT (*J. Biol. Chem.*, 1923, **58**, 267—284).—Determinations have been made by Van Slyke and Palmer's method (A., 1920, ii, **131**) of the organic acid content of the urine of eight normal women. Under normal conditions, values (uncorrected for creatinine) equivalent to 6·8—10 c.c. of 0·1*N*-acid per kg. per day, which are similar to those obtained by Van Slyke and Palmer (A., 1920, i, 459) for men, were obtained. The amount excreted per hour by day (*i.e.*, during activity) was much greater than that by night. During fasting, the hourly excretion was equivalent to 15—24 c.c. of 0·1*N*-acid. This was markedly increased by diets rich in fruit or protein, but was only slightly affected by diets poor in these substances. One-third to one-half of the acids titrated by the above method consists of uric

acid, creatinine, creatine, and amino-acids. Diets which increase the organic acid excretion also increase that of uric acid. E. S.

Creatinine Excretion of Women. L. McLaughlin and K. Blunt (*J. Biol. Chem.*, 1923, **58**, 285—290).—Determinations of the creatinine coefficients of eight normal women gave values (6·3—9·6 mg. of creatinine nitrogen per kg. per day) similar to those obtained by others for men. The higher values were obtained in the case of women who were below normal weight. There was no regular difference between the amounts excreted by day and those excreted by night. Creatine was almost invariably present in the day urine of one healthy woman. E. S.

Excretion of Ammonia and Nitrogen. R. S. Hubbard (*J. Biol. Chem.*, 1924, **58**, 711—719).—As the experiments of Marshall and Crane (A., 1923, i, 628) led to different conclusions from those drawn by Hubbard and Munford (A., 1923, i, 169) by a statistical examination of the results of analyses of human urine, a more extended series of figures has been obtained and examined as before. The results in general confirm the conclusions of Hubbard and Munford as to the excretion of ammonia by normal human subjects. G. M. B.

Effect of Injections of Sodium Phosphates and Sodium Hippurate upon the Excretion of Acid and Ammonia by the Kidney. B. M. Hendrix and J. P. Sanders (*J. Biol. Chem.*, 1923, **58**, 503—513).—Injections of disodium hydrogen phosphate or of sodium hippurate in fasting dogs cause an increase in the titratable acidity and in the ammonia content of the urine, the sum of these increases being practically equivalent to the salts injected. The results obtained support the view of Nash and Benedict (A., 1922, i, 191) that a portion of the urinary ammonia is formed in the kidney, but it is suggested that part may have its origin in the intestine. The kidney can probably retain sodium from sodium salts of acids as strong as hippuric acid, but is unable to do so in the case of much stronger acids. E. S.

Spontaneous Crystallisation of Uric Acid from Urine. L.-C. Maillard (*Bull. Soc. Chim. biol.*, 1923, **5**, 930—934).—It has been thought by some authors that uric acid is soluble in urine because it exists therein as a complex compound. The present author refers to an observation of his that uric acid crystallises spontaneously from urines which are markedly acid and show a high formol titration figure. He suggests that this may indicate that the compound mentioned above may be of the nature of an amino-acid complex. C. R. H.

Natural Porphyrins. V. Coproporphyrin in the Urine and Serum in Normal and Pathological Conditions. H. Fischer and W. Zerweck (*Z. physiol. Chem.*, 1924, **132**, 12—33).—Urine (1000 parts) is made acid with acetic acid (3 parts) and extracted with ether (1000 parts). The ether is washed with water (20 parts) and extracted with 25% hydrochloric acid (3 parts)

and the solution observed spectroscopically. Coproporphyrin, if present, shows bands with centres at λλ *ca.* 592, 548, and 491. To the acid solution, ether, sodium acetate, and sodium hydroxide solution are added so that the mixture is still acid with acetic acid. The ethereal solution is then washed, and if coproporphyrin is present, it shows bands at λλ *ca.* 624, 567, 528. The coproporphyrin may be again extracted with acid and observed. Coproporphyrin has been found in the urine of normal individuals independently of whether their food has contained flesh or blood (cf. Schumm, A., 1923, i, 631, who found porphyrin present in normal subjects only after flesh or blood was consumed). From the united ethereal extracts, a solution containing cotporphyrin methyl ester, identified spectroscopically, was prepared. Coproporphyrin has been identified in the urine of guinea-pigs, in normal human serum, and in the serum of the horse, ox, and fowl. Investigations of the porphyrin in blood and urine in certain pathological conditions in man, as pernicious anæmia, hæmolytic icterus, and urobilinuria, are described. W. O. K.

Hæmatoporphyria Congenita. IV. The Identification of Natural Porphyrins in Serous Fluids and in Organs. O. Schumm (*Z. physiol. Chem.*, 1924, **132**, 62—71).—By means of spectroscopic observations, the presence of urinoporphyrin and of cotporphyrin has been detected in the pleural exudate from a patient suffering from hæmatoporphyria congenita. Details are given of the methods to be followed in examining such fluids or organs for the presence of porphyrins. W. O. K.

Hæmatoporphyrin of Human Fæces. A. Papendieck (*Z. physiol. Chem.*, 1924, **133**, 97—99).—Polemical. S. S. Z.

Ether Extract of Fæces. A. D. Holmes and R. H. Kerr (*J. Biol. Chem.*, 1923, **58**, 377—381).—Experiments made in connexion with the digestibility of edible fats indicate that the amount of unutilised fat excreted in the fæces in the form of soaps is insignificant. Further, the ethereal extract of the fæces appears to be of a uniform composition independent of the particular fat ingested. E. S.

Decolorisation of Ethereal Extracts. J. Markoff (*Compt. rend. Soc. Biol.*, 1923, **89**, 113—115; from *Chem. Zentr.*, 1924, i, 80).—Directions are given for the use of phosphotungstic acid for decolorising ethereal extract of fæces. Preliminary removal of the ether by distillation is necessary. G. W. R.

Adsorption and the Distribution of Drugs in the Organism. III. E. Keeser (*Biochem. Z.*, 1924, **144**, 536—544).—There is no parallelism between the adsorption capacity of charcoal for alkaloids and iodine *in vitro* and its detoxicating effect in the intestinal tract of the dog. The method by which a charcoal is prepared and not its origin is the determining factor of its adsorptive capacity. Strychnine nitrate is adsorbed more readily than morphine hydrochloride. In the presence of sodium bi-

carbonate, morphine hydrochloride and strychnine nitrate are adsorbed to a higher extent by charcoal. The electric charge changes in blood charcoal (Kahlbaum) at p_H 3·5, in beech charcoal (Kahlbaum) at p_H 6·6, in "carbovent" at p_H 3·9. There is no change in the electric charge in bone charcoal (Kahlbaum), beech charcoal (Merck), and lime tree charcoal (Kahlbaum) at the investigated range of hydrogen-ion concentration. S. S. Z.

Action of Different Substances, particularly the so-called Heart Remedies, on Disturbances of the Rhythm of the Heart. W. Simon (*Arch. Pharm. Exp. Ther.*, 1924, **100**, 307—315).—Only caffeine, calcium salts, human serum, and especially adrenaline, out of a large number of substances investigated, were able to relieve the disturbance of the rhythm of an isolated frog's heart, caused by cocaine or strychnine. W. O. K.

Physico-chemical Technique for Detection of Polonium injected into Organs. (Mme.) J. S. Lattès and A. Lacassagne (*Compt. rend.*, 1924, **178**, 630—632; cf. this vol., i, 347).—The organ into which polonium has been injected is treated with potassium chlorate and hydrochloric acid until destroyed (fats, unaffected by this reagent, may then be separated mechanically); the solution obtained is boiled in presence of silver foil, and the polonium deposited on the latter determined by measuring its activity. This method is much more sensitive than the autohisto-radiographic method, but obviously gives only the mean polonium content of an organ and not the distribution of that element. E. E. T.

Influence of "Alkaloids" on Permeability. W. Heubner (*Biochem. Z.*, 1924, **144**, 351—352).—The suggestion is made that the observations of Brinkmann and Szent-György (A., 1923, i, 974) on the action of morphine and codeine salts on the permeability of a collodion membrane to hæmoglobin, may have had their origin in the action of the anion; the work of Rhode (A., 1922, i, 1088) on the action of morphine chloride and codeine phosphate on hæmolysis is cited in this connexion. J. P.

Vasodilatation by Amino-acids in Isolated Dog Kidneys. H. Fredericq and L. Brouha (*Compt. rend. Soc. Biol.*, 1923, **89**, 665—667; from *Chem. Zentr.*, 1924, i, 213).—Glycine, *l*-leucine, *d*-alanine, and *dl*-valine exert a vasodilatory effect in isolated dog kidneys, which is demonstrated by the increased flow of liquid from the renal vein and the ureter. The action of *dl*-phenylalanine is less definite. G. W. R.

Effect of Amino-acids on Exchanges in Isolated Organs. H. Fredericq and L. Mélon (*Compt. rend. Soc. Biol.*, 1923, **89**, 668—669; from *Chem. Zentr.*, 1924, i, 213; cf. preceding abstract).—Isolated dog kidneys were perfused with Locke solutions containing 0·5% of different amino-acids. The first result was the production of an acid reaction, an effect not observed with Locke solution alone. *d*-Alanine and *l*-leucine cause an increase in

nitrogen titratable by formaldehyde in the liquid. Other compounds have no effect or depress the amount of nitrogen titratable by formaldehyde. G. W. R.

Detection of Toluene in Organs and its Distribution in the Organism. S. KURODA (*Biochem. Z.*, 1924, **144**, 287—293).—The toluene is distilled from a suspension of the organ in water and collected in carbon tetrachloride. It is nitrated, dissolved in water, made alkaline with sodium hydroxide, extracted with ether, and finally weighed. After toluene poisoning, the central nervous system of dogs and guinea pigs contains more toluene than the other organs, with the exception of the spleen, and the leucocytes of the blood are diminished. J. P.

Effect of Chloroform and Phosphorus Poisoning on Carbohydrate Tolerance. M. BODANSKY (*J. Biol. Chem.*, 1923, **58**, 515—522).—Experiments on dogs indicate that the lævulose tolerance test described in this paper is of great value in measuring the degree of liver injury during chloroform and phosphorus poisoning. Dextrose and galactose are not suitable for this purpose. E. S.

Action of Hydrazine and some of its Derivatives in producing Liver Injury as measured by the Effect on Lævulose Tolerance. M. BODANSKY (*J. Biol. Chem.*, 1924, **58**, 799—811).—The degree of liver injury produced in dogs by hydrazine and a number of derivatives have been determined by the lævulose tolerance test previously described (cf. preceding abstract), and the results confirmed by *post-mortem* examination. Hydrazine, phenylhydrazine, *s*-di*iso*propylhydrazine, and ββ-azopropane ($CHMe_2{\cdot}N{:}N{\cdot}CHMe_2$) are highly injurious to the liver, whereas methylphenylhydrazine, diphenylhydrazine, acetylphenylhydrazine, and *p*-hydrazinobenzoic acid have much less effect. G. M. B.

Influence of Hydrazine on Blood Concentration and Blood-sugar Content. F. P. UNDERHILL and S. KARELITZ, jun. (*J. Biol. Chem.*, 1923, **58**, 147—151).—The hypoglycæmia produced in dogs by the subcutaneous injection of hydrazine hydrate (cf. A., 1914, i, 632; 1915, i, 1037) is preceded by a transitory condition of hyperglycæmia; no sugar, however, appears in the urine. Hydrazine poisoning also causes a marked increase in blood concentration, which is ascribed both to the loss of fluid and to the inability of the animal to retain food or water; this effect probably contributes largely to the fatal results. There is no direct relationship between the degree of blood concentration and the extent of hypoglycæmia. E. S.

Specificity of the Intracellular Hydrogenases in Frog's Muscle. M. E. COLLETT (*J. Biol. Chem.*, 1924, **58**, 793—797).—The influence of certain protoplasmic poisons on the oxidation of citric and succinic acids by washed frog's muscle in presence of methylene-blue has been examined. The action is more readily inhibited by phenol and chloral hydrate in the case of the oxidation

of citric acid than in that of succinic acid: this order is reversed with poisons such as tellurites, selenites, selenates, and arsenates. The conclusion is drawn that there are two enzymes specific for the oxidation of citric and succinic acids, respectively.

G. M. B.

Fungal Product, $C_6H_6O_4$, and its Behaviour on Hydration. N. WIJKMAN (*Z. physiol. Chem.*, 1924, **132**, 104—108).—When *Aspergillus* spp. are grown on a medium containing sucrose in quartz or paraffined glass flasks and the acidity of the medium is kept within certain limits, there regularly separate from the culture liquid crystals of a *substance*, which after sublimation under a low pressure melts at 154° and possess the formula $C_6H_6O_4$ [*copper* salt, $(C_6H_5O_4)_2Cu,H_2O$; *acetyl* compound, $C_6H_4O_2(OAc)_2$]. On treatment with hydrogen in presence of a catalyst, a compound, m. p. 80—90°, b. p. *ca.* 200°/1 mm., is obtained, which appears to be hydroglucal, although this has not been proved conclusively.

W. O. K.

Simultaneity of Two Contradictory Toxic Effects (Immunity and Anaphylaxis) on the Same Cell. C. RICHET, (MLLE.) E. BACHRACH, and H. CARDOT (*Compt. rend.*, 1924, **178**, 535—537).—The lactic acid bacillus, if cultivated in presence of copper sulphate (or of mercuric chloride) and potassium arsenate together, acquires simultaneously sensitivity towards the former and immunity towards the latter. E. E. T.

Diphtheria Toxin and Anatoxin. Flocculating Power and Immunising Properties. G. RAMON (*Ann. Inst. Pasteur*, 1924, **38**, 1—10).—Antidiphtheria serum produces a flocculation when added to diphtheria toxin. The amount of antitoxin required to cause flocculation measures the toxicity of the toxin. When diphtheria toxin, to which formalin (3 or 4 parts per 1000) had been added to prevent bacterial contamination, was kept at 40—42°, it lost its toxicity, but retained its property of being flocculated by antitoxin. The *anatoxin* so produced retains also the immunising power, *in vivo*, of the original toxin, and its strength may be estimated by finding the amount of antitoxin required to cause flocculation, as this has been found experimentally to be proportional to its immunising effect. W. O. K.

Antiseptic Value of Hexamethylenetetramine *in vitro*. A. DUTHOIT (*Compt. rend. Soc. Biol.*, 1923, **89**, 656—658; from *Chem. Zentr.*, 1924, i, 71).—With 2% hexamethylenetetramine in Ringer solution, paratyphoid and typhoid bacilli are completely killed in 4—7 days. *Bacillus coli* and pneumobacilli are not completely killed, even after 10 days. The antiseptic effect of hexamethylenetetramine does not reside in the formaldehyde group.

G. W. R.

Antiseptic Effect of Hexamethylenetetramine. A. DUTHOIT (*Compt. rend. Soc. Biol.*, 1923, **89**, 658—660; from *Chem. Zentr.*, 1924, i, 71; cf. preceding abstract).—Data are given for the bacteri-

cidal effect of the gall of dogs on different species of bacteria with and without preliminary injection of hexamethylenetetramine. It is found that hexamethylenetetramine is less effective as an antiseptic *in vivo* than *in vitro*. G. W. R.

Effects of Electrolysis on Animal Tissue Enzymes. Abundance of Silicic Acid in the Ash. F. MAIGNON (*Compt. rend.*, 1924, **178**, 654—657).—The enzymes from all body-tissues examined contained silica and calcium. Some tissue enzymes also contained characteristic quantities of phosphorus, arsenic, magnesium, and iron. Electrolysis of the enzyme preparations in aqueous solutions gave a coagulum at both anode and cathode with concomitant loss of therapeutic properties (cf. this vol., i, 350). E. E. T.

Rapid Analysis of Sugars. Purification and Concentration of Enzyme Solutions. F. W. REYNOLDS (*Ind. Eng. Chem.*, 1924, **16**, 169—172).—Yeast extracts may be freed from colour and substances causing turbidity by dialysing or by washing on an ultra-filter and subsequently acidifying with acetic acid, whereby the substances causing turbidity are flocculated and can be removed by filtration through paper. Highly active preparations of invertase and melibiase may be obtained by concentrating crude or purified yeast extracts by ultra-filtration. A simple ultra-filter with a collodion membrane is described and illustrated. The impurities, especially those which are optically active, are largely eliminated and not concentrated with the enzyme. The activity of enzymes prepared by these means was about eight times that of the ordinary yeast extracts, and was such that sucrose solutions could be completely hydrolysed with their aid in 15 minutes at the ordinary temperature. Ultra-filtration should be useful as a means of concentrating other enzymes for use as analytical reagents and also in the study of the enzyme action of plant and fruit juices. H. C. R.

Purification of Toxins, Ferments, and other active Biological Organic Colloids. L. MICHAELIS and H. DAVIDSOHN (*Biochem. Z.*, 1924, **144**, 294—297).—Details are given of the patented process (1912) used for purifying toxins, ferments, etc., by precipitation at the isoelectric point or at a definite hydrogen-ion concentration. J. P.

Mechanism of Alcoholic Fermentation. III. A. LEBEDEV (*Z. physiol. Chem.*, 1924, **132**, 275—296).—Yeast incubated with sucrose in the presence of sodium sulphite and sodium or potassium dihydrogen phosphate, yields compounds the osazones of which (m. p. 202—209°) are free from phosphorus, but in the presence of these phosphates alone the osazones obtained (m. p. 143—152°) are those of phosphate esters differing from hexose biphosphate, whilst the presence of disodium or dipotassium hydrogen phosphates may or may not lead to the formation of a phosphate ester, the results varying with different yeast preparations. Whilst the analyses of the various phosphate esters has not yet been com-

pleted, it is apparent that it is possible to control, not only the amount, but also the nature of the hexose phosphate formed during yeast fermentation. The author supposes yeast fermentation to proceed in acid solution as follows: hexose → two trioses → glyceric acid → pyruvic acid → acetaldehyde → alcohol → carbon dioxide, whilst in neutral or alkaline solutions glycerol is formed along with glyceric acid and acetic acid accompanies alcohol. The formation of the four known hexose phosphates (including the new osazone-forming monophosphate described by the author) is correlated with the preliminary formation of glyceraldehyde, dihydroxyacetone, and the two corresponding monophosphates of these compounds. In accord with the author's views the presence of nine individual enzymes in the zymase complex is postulated. J. P.

Influence of Amines on Fermentation. II. J. ORIENT (*Biochem. Z.*, 1924, **144**, 353—360).—The effect of various alkylamines and their salts, glucosamine and its hydrochloride, diamines, and indole derivatives on yeast fermentation has been investigated. In general the salts of amines and diamines increase, whilst the free bases diminish fermentation. Indole has a slight inhibiting action, whilst scatole has the reverse effect (cf. A., 1923, i, 171). J. P.

Action of Drugs containing Hydroxymethylanthraquinones on Fermentation. J. ORIENT (*Biochem. Z.*, 1924, **144**, 361—365).—The action of various pharmacological preparations of *Rheum*, *Aloe*, *Senna*, *Cascara*, *Frangula*, *Cassia*, *Jalappa*, and *Colocynthis* on yeast fermentation has been investigated. In general fermentative action is increased, more especially by the rhubarb group rich in hydroxytrimethylanthraquinone. J. P.

Fermentation with Non-ferments. W. BIEDERMANN (*Z. angew. Chem.*, 1924, **37**, 71—73).—If a solution containing diastase (*e.g.*, saliva or a solution of saliva albumose) is heated, a turbidity appears at 70—80°, owing to partial coagulation of the "zymogen," and the diastatic power is considerably diminished; it does not, however, disappear even by heating the solution to boiling, and may be considerable in the presence of oxygen. This regeneration by means of air is further enhanced by the presence of the above coagulate. A solution of saliva ash, or even simple salt solutions (particularly sodium chloride), can produce a slow degradation of amylose to sugar, although here again thorough aëration is necessary. The activity of the salts is increased, not only by the specific protein, but also by the inactive degradation products, the presence of amino-acids (*e.g.*, glycine, leucine) being found advantageous. It appears that the organic ferment, and not the inorganic substance, should be regarded as the activator. Treatment of fibrin with steam yields solutions which, after addition of sodium chloride or a suitable phosphate mixture, are capable of fermenting amylose, if an adequate supply of air is maintained. By employing very dilute ferment solutions amylose can be converted into dextrin alone, without a simultaneous production of sugar. It may,

finally, be said that, below a certain dilution, small quantities of saliva diastase have exactly the same action as the "complementary" inorganic salts alone, provided the latter are in a corresponding concentration. W. T. K. B.

Comparison of the Action of Acids and Enzymes in Hydrolytic Phenomena. H. COLIN and A. CHAUDUN (*J. Chim. physique*, 1923, **20**, 471—483).—The hydrolysis of sucrose by diastase is considered theoretically and it is shown that the velocity of the reaction does not increase with the concentration of the sucrose (a) nor with the concentration of the diastase (n), but rather with the ratio of these concentrations, a/n. The condition under which the reaction follows Wilhelmy's law is that a/n shall be less than a value a'/n' which is characteristic of the solution of diastase employed. When $a/n<a'/n'$ then the amount of sucrose transformed each instant can be calculated by Wilhelmy's formula $x=a(1-e^{-kt})$, which means that under these conditions the rates of hydrolysis by acids and diastase are identical. When $a/n>a'/n'$ the initial velocity $v=f(an)$ is independent of a and proportional to n. These facts indicate that the enzyme forms a complex with the sugar, which then decomposes with a finite velocity in keeping with the law of mass action. The above statements apply exactly to the action of emulsin on glycosides. The velocity of inversion by diastase decreases with increasing viscosity of the solution, but in the case of hydrolysis with acids the viscosity appears to have no influence on the velocity of the change. J. F. S.

Inactivation of Invertase in Fresh Yeast by Silver Nitrate. H. VON EULER and E. WALLES (*Z. physiol. Chem.*, 1924, **132**, 167—180).—The invertase of yeast-cells is inactivated by silver nitrate as the latter is taken up from the solution by the cells. It may regain its activity by self-regenerative processes or by treatment with hydrogen sulphide. The phenomenon is therefore parallel to the inactivation of yeast enzymes in solution (Euler and Myrbäck, A., 1922, i, 959). Yeast inactivated by silver nitrate and regenerated by treatment with hydrogen sulphide shows, after incubation, an increased activity. Owing to these protective mechanisms the invertase of the living yeast-cell is two hundred times more resistant to the toxic action of silver than is the same amount of the enzyme in solution. Zymase is much more susceptible to inactivation by silver than is invertase. J. P.

Invertase. III. H. VON EULER and K. JOSEPHSON (*Ber.*, 1924, **57**, [*B*], 299—302; cf. A., 1923, i, 721).—The maximum purification of invertase preparations by the author's methods appears to be reached when the value If^0 attains about 250.

Determinations of the molecular weight of invertase by measurements of diffusion indicate that the "active group" is contained in or associated with a complex of molecular weight about 20,000.

Specimens of invertase have been obtained in which the ash does not exceed 0·13%; the higher ash content of previous preparations is therefore due to impurities. The acidic and basic dissociation

constants have been determined provisionally to be $K_a=10^{-7}$ and $K_b=10^{-11}$, respectively. The isoelectric point of invertase at 20° is calculated to be at p_H 5. H. W.

Affinity of Invertase for Different Sugars. H. VON EULER and K. JOSEPHSON (*Z. physiol. Chem.*, 1924, **132**, 301—327).—At p_H 4·5 invertase of bottom yeasts has a marked affinity for both α- and β-dextrose, the affinity being slightly greater in the latter case than in the former. The affinity for lævulose is of the same order as for dextrose. In contrast to the findings of Kuhn (*Z. physiol. Chem.*, 1923, **127**, 234; **129**, 57), no general support is forthcoming for the view that separate "gluco-" and "fructo-" invertases exists. The affinity of invertase for other hexoses and pentoses depends on the presence of a free reducing group (aldehydic or ketonic) and on the configuration of the remainder of the molecule, which may be considerably modified without entirely abolishing the affinity. In general, the β-forms of the hexoses and pentoses show a greater affinity than the α-forms except in the cases of dextrose and xylose, where both stereoisomerides react practically alike. A relation appears to exist between the configuration of the sugar molecule and the relative affinity of invertase for its α- and β-forms; thus the pairs dextrose–xylose and galactose–arabinose give parallel results. The affinity of invertase for the disaccharides has also been studied but no very definite conclusions are drawn. J. P.

Uniformity in Invertase Action. J. M. NELSON and F. HOLLANDER (*J. Biol. Chem.*, 1923, **58**, 291—304).—The abnormality observed with certain invertase preparations (A., 1922, i, 388) has been shown to be due to inactivation. Thus, when the abnormal preparations were incubated at 25° with a citrate buffer mixture at p_H 4·5 (the acidity at which the abnormality was observed) some loss of activity occurred, whilst this was not the case with normal preparations. Further, addition of sodium chloride or of boiled normal invertase prevented inactivation in the case of the preparation which was rendered normal by this treatment, but did not do so with the second abnormal preparation, which could not be rendered normal in this way. At 25° the point of maximum stability of one abnormal and two normal invertase preparations was found to lie, not at the acidity for maximum activity (p_H 4·5; cf. Euler and Laurin, A., 1920, i, 506), but on the alkaline side of this (about p_H 5·8). E. S.

Enzyme Adsorption. I. A Contribution to the Knowledge of "Invertin" of Willstätter and his Collaborators (*Z. physiol. Chem.*, 1924, **133**, 1—21).—The adsorption curve obtained by adsorbing the invertase of autolysed yeast juice with aluminium hydroxide deviates from the normal adsorption isotherm. The author argues that this is due to the interference of impurities adsorbed from the juice. Any change in the initial activity of an impure juice yields a different adsorption curve. In certain cases, it is even possible for aluminium hydroxide

to adsorb more of the enzyme out of dilute impure solutions than out of similar solutions of higher concentration. The adsorption value rises with the purity of an invertase preparation. S. S. Z.

Influence of Alkaloids of the Atropine, Cocaine, and Morphine Groups on Yeast Invertase. P. Rona, C. van Eweyk, and M. Tennenbaum (*Biochem. Z.*, 1924, **144**, 490—519).—A series of alkaloids of the above groups have been found to possess an inhibiting influence on the action of yeast invertase. Although the intensity of the inhibition varies with the various alkaloids, the general inactivating influence proceeds logarithmically according to the concentration of the alkaloid present. The inhibition is reversible, and is influenced by the hydrogen-ion concentration of the medium. No connexion exists between the optical configuration and the inhibitory power of *dl*-atropine and *l*-hyoscyamine; *l*-cocaine and *dψ*-cocaine; and *l*-ecgonine and *d*-ecgonine. In none of these three cases was there any difference between the inhibitory power of the isomers. Tropine inhibits much less markedly than atropine, whilst tropic acid does not inhibit at all; nor does an equimolecular mixture of tropine and tropic acid have a greater inhibiting effect than tropine alone. *d*- and *l*-Ecgonine do not inhibit, but, on the other hand, the chemically-related cocaine does. The substitution of the hydrogen of morphine by the methyl group (codeine) produced no apparent change in inhibitory power, but substitution by ethoxyl (dionine) produced a small though definite change. S. S. Z.

Heat and Radiation Inactivation of Malt Amylase. H. Lüers and P. Lorinser (*Biochem. Z.*, 1924, **144**, 212—218).—The zone of maximal thermostability of malt amylase is displaced towards higher p_H values by increased concentration of an acetate buffer. Gelatin, egg-albumin, and gum arabic protect the amylase from heat inactivation especially between p_H 6·0 and 7·0, and produce a flattening of the zone of maximum stability. Maltose has a similar protective influence and a direct proportionality exists between log $C_{maltose}$ and the coefficient of inactivation. The inactivation of amylase by ultra-violet radiation follows neither the mono- or bi-molecular equation, nor the Schütz law. The effect of alterations in the hydrogen-ion concentration is much less marked in this case than in that of heat-inactivation. The temperature coefficient for ultra-violet inactivation is k^{30}/k^{20} 1·30, and physicochemically the two methods of inactivation are dissimilar. J. P.

Ferments and Light. IV. Diastase. III. L. Pincussen and F. di Renzo (*Biochem. Z.*, 1924, **144**, 366—371; cf. A., 1924. i, 107).—The inactivation by ultra-violet light of 0·1% of malt diastase acting on 1% starch solution at varying p_H proceeds as a unimolecular reaction, whilst in the presence of 0·5% of starch only the later stages correspond with the unimolecular equation. The departure from the simple equation is still more marked in the presence of 0·25% of starch. A 0·2% solution of the enzyme gives complex results in the presence of 1·0, 0·5, and 0·25% starch solutions. J. P.

Ferments and Light. V. Diastase. IV. L. PINCUSSEN (*Biochem. Z.*, 1924, **144**, 372—378).—Sodium chloride protects both the diastase and maltase in malt diastase from inactivation by exposure to sunlight. *M*/6-Phosphate solution protects malt diastase and the maltase of "pancreatin Rhenania" from inactivation by ultra-violet light, whilst more dilute phosphate solutions are less effective. Similar results are given by acetate solutions of the same p_H. In the presence of a phosphate buffer, with or without the addition of sodium chloride, the protective action is at a maximum at p_H 6·64. Ammonium, potassium, and lithium chlorides, potassium bromide, and sodium fluoride protect taka-diastase from ultra-violet light to varying degrees, an effect which is more marked in dilute solutions of these salts than in more concentrated solutions. Potassium and sodium nitrates and nitrites give similar results but do not show the same varying effects at different temperatures. J. P.

Purification of Ferments by Electro-dialysis and Electro-Osmosis. I. Malt Diastase. R. FRICKE and P. KAJA (*Ber.*, 1924, **57**, [*B*], 310—313).—Electro-dialysis of solutions of malt diastase is effected in a cell divided into three compartments by collodion membranes. The central compartment contains the solution of malt diastase, whilst the outer compartments contain distilled water and the iron gauze cathode and carbon anode, respectively. The voltage used is 220 or 22. As soon as the current has attained a strength of 0·0045—0·006 amp. per sq. cm. the solution in the outer cells is replaced by distilled water and the process is repeated until the current strength remains practically constant at its initial value after recharging the anode and cathode cells. The dry matter concentration of the solution of malt diastase is very considerably lowered, whilst the activity of the enzyme towards starch is increased 2·1 to 2·5 times. After concentration by cautious freezing, the diastase solution gives slight protein but marked carbohydrate reactions. The ash is diminished from 5% to 1%, the nitrogen content from 6·14% to 3·51%.

Electro-osmosis is conducted in a five-compartment cell in which the extreme compartments which contain the electrodes are separated from the intermediate compartments by collodion membranes impermeable to diastase. The barrier between the intermediate and central cells is of collodion permeable to diastase. The central compartment contains the malt diastase solution, the others contain water. The pressure used is 22 volts. After electro-osmosis during 5 days, 39% of the malt diastase remains in the central compartment and shows a diminution in activity from 2·4 to 0·8, 32% has passed towards the anode and is inactive towards starch, 16% has passed towards the cathode and has increased in activity from 2·4 to 4·6, whilst 13% remains in the membranes. The highly active malt diastase gives a marked positive reaction for carbohydrates; it contains carbon 56·4%, hydrogen 7·9%, and nitrogen 3·28%. H. W.

Non-homogeneity and other Properties of Malt Diastase. R. Fricke and P. Kaja (*Ber.*, 1924, **57**, [*B*], 313—316).—A comparison of the starch-liquefying and saccharifying powers of Merck's "diastase absolut" with those of preparations purified by the authors' methods (preceding abstract) shows these properties to be affected to the same degree with respect to soluble starch; the purified product, however, appears to be relatively deficient in starch-liquefying power towards potato starch, thus supporting von Euler's hypothesis ("Chemie der Enzyme," II, 1922, 116) that at least two components are present in malt diastase. The previous conclusion that the presence of proteins in crude malt diastase is not essential to its diastatic properties is strengthened by the observation that the ferment is not affected by prolonged treatment with trypsin. Uranyl acetate is harmless as long as proteins are present with which it forms a precipitate, but after this point is passed, it acts as a vigorous poison. H. W.

Amylolytic and Glycolytic Enzymes of the Pancreas and the Salivary Glands. C. Serono and A. Cruto (*Rass. Clin. Terap. Sci. aff.*, 1923, **22**, 139—142; from *Chem. Zentr.*, 1924, i, 62).—A glycerol extract of pancreas, an aqueous extract of dried sterilised pancreas powder, or salivary diastase, does not form maltose or dextrose from starch solution, but only *iso*maltose. The amount of *iso*maltose formed depends on the concentration of starch. The amylolytic enzyme from pancreas, after separation from lipolytic and proteolytic enzymes, is unstable, but can be stabilised by the addition of plant colloids to the solution. The presence of colloidal material increases the stability to heat of the pancreatic and salivary enzymes. The glycolytic enzyme obtained from the pancreas (Serono and Cruto, *Arch. Farm. Sperim.*, 1913, **14**, 501) is held to be an inner enzyme liberated by maceration, and may be obtained from other tissues in the same way. Only small quantities of ethyl alcohol and carbon dioxide are obtained by its action. It is concluded that no enzyme capable of synthesising sugar occurs in the pancreas. Glycogen is probably formed from *iso*maltose and not from the polymerisation of dextrose. Liver glycogen is only slightly attacked by pancreatic extract under aseptic conditions. G. W. R.

Presence of Inulase in Takadiastase. Y. Takahashi (*Biochem. Z.*, 1924, **144**, 199—202).—Takadiastase contains an inulase capable of hydrolysing inulin to lævulose. J. P.

Inulin and Inulase. IV. H. Pringsheim and G. Kohn (*Z. physiol. Chem.*, 1924, **133**, 80—96).—When inulin is heated in glycerol it is "dissociated" into polymers which consist of 8—10 monoses. Such "dissociated" inulin gradually acquires the properties of "associated" inulin when in solution and eventually separates out as such. The most favourable reaction for the action of inulase on inulin is p_H 3·8, and the hydrolysis proceeds according to the formula of a unimolecular reaction.

Press juices of inulase obtained from older moulds (*Aspergillus niger*) were more active than those derived from younger moulds. The reaction constants have been worked out for inulins of various degrees of purity and for "dissociated" inulin (obtained by heating inulin in glycerol). Invertase hydrolyses inulin and "dissociated" inulin at a hydrogen-ion concentration of the order of that of gastric juice. *Aspergillus niger* contains an invertase as well as an inulase. S. S. Z.

Polysaccharides. XXII. Lichenase and Reserve Cellulose (Lichenin). P. KARRER, M. STAUB, A. WEINHAGEN, and B. JOOS (*Helv. Chim. Acta*, 1924, **7**, 144—154).—Lichenin, which has already been recognised as a form of cellulose (A., 1923, i, 1182), is now identified with so-called reserve cellulose. It follows that the enzyme lichenase is closely related to cytase. Since the latter, however, contains enzymes which attack not only reserve celluloses but mannan and galactan, the term lichenase is retained for the enzyme obtained from the snail, *Helix pomatia*. The crude snail extract contains, besides lichenase, a variety of other enzymes, including invertase, lipase, diastase, inulase, maltase, and a cellobiase. The lichenase can be purified from the accompanying enzymes by dialysing, since all of them, with the exception of cellobiase, are unstable in water and quickly disappear. Some of the lichenase is lost during the purification, since it can diffuse through a membrane. The lichenase is best isolated by precipitation from the dialysed solution with acetone. The enzyme rapidly loses its activity if heated above 36°. The most active lichenase preparations are those which have not passed through a drying stage. Basic aluminium sulphate adsorbs lichenase almost completely from neutral solution; the enzyme can be brought into solution again by potassium dihydrogen phosphate and the solution so obtained can be purified by dialysis. Aluminium hydroxide also adsorbs the enzyme completely, but recovery is not so good as from the basic sulphate. The activity of lichenase solutions is not affected by sodium chloride, albumin, or soap, but is lowered by all sugars. The work of Pringsheim and Seifert (A., 1923, i, 998) indicates the presence of lichenase in barley, and it appears to be present in many other plants. Plant lichenase is, however, difficult to separate from accompanying enzymes. E. H. R.

Polysaccharides. XXIII. Separation of Lichenase into Constituent Enzymes. P. KARRER, M. STAUB, and B. JOOS (*Helv. Chim. Acta*, 1924, **7**, 154—159).—When a snail lichenase preparation is preserved, its activity gradually diminishes in the course of about 14 days by some 30%, and then remains constant for a long period. The change is shown to be due to the disappearance of cellobiase, a constituent enzyme. Whereas fresh lichenase decomposes lichenin or cellobiose completely to dextrose, lichenase which has been preserved only carries the decomposition of lichenin to an intermediate stage, probably to cellobiose.

E. H. R.

Serum Lipase. G. FANCONI (*Fermentforsch.*, 1924, **7**, 307—348).—Some hydrolysis of fats and cholesterol esters is shown to occur in human serum. Since the tributyrinase of serum (the so-called serum lipase) can be extracted in part by fats and lipoids, and since in lipæmic serum the lipolytic activity is less than in that from the fasting animal, it is argued that the tributyrinase is probably identical with the fat-splitting agent of the serum. The view that serum lipase and complement are closely related is not supported by the fact that quinine and atoxyl inhibit the lipolytic activity but not the complement function of serum. The variations in the lipolytic activity of serum in physiological and pathological conditions are described. R. K. C.

Action of Arsenic and Antimony Compounds on the Fermentative Functions of the Organism. II. Action of certain Arsenic and Antimony Preparations on Pepsin. J. A. SMORODINCEV and N. P. RIABOUSCHINSKY (*Biochem. Z.*, 1924, **144**, 26—30).—Sodium and potassium arsenites and arsenates, and potassium antimonyl tartrate retard the action of pepsin on casein, the last-mentioned in $N/50$, the others in $N/40$ solutions. Lower concentrations of these salts from $N/80$ to $N/10240$ have no influence on the activity of pepsin. In contrast to ptyalin (A., 1923, i, 1246), pepsin is not so susceptible to antimony as to arsenic, and is more stable to both types of compound than is the former enzyme. Hydrochloric acid ($N/40$ to $N/1600$) and tartaric acid ($N/10$ to $N/1280$) have no influence on the action of pepsin. J. P.

Adsorption of Trypsin by Filter-paper. TSOU-HIA HSÜ (*Biochem. Z.*, 1924, **144**, 303—307).—Trypsin (Merck) is adsorbed from solution by various makes of filter-paper (Schleicher and Schüll, Dreverhoff). The adsorbed enzyme may be partly recovered by washing with dilute sodium hydroxide and with phosphate solutions of p_H 6·6 to 7·6. Washing with acid, sodium carbonate, and ammonia is ineffective. Variations in temperature have little or no effect on the extent of the adsorption. J. P.

Influence of Colloids on Enzymes. III. I. HAGIHARA (*Biochem. Z.*, 1924, **144**, 482—489).—Cholesterol has no influence on the action of trypsin at the hydrogen-ion concentration range p_H 5·3—p_H 10·6. Lecithin, on the other hand, stimulates the action of the enzyme in proportion to the quantity present. This stimulation occurs only in alkaline solutions, being entirely absent at or below p_H 6·8; it reaches its maximum at p_H 7·6 and falls in more alkaline solutions. S. S. Z.

Kinetics of Trypsin Digestion. I. Experimental Evidence Concerning the Existence of an Intermediate Compound. J. H. NORTHROP (*J. Gen. Physiol.*, 1924, **6**, 239—243).—If, as has been suggested, a compound is formed between trypsin and its substrate, the presence of gelatin should decrease the rate of hydrolysis of casein, but this was found not to be the case. This result cannot be explained on the hypothesis that different enzymes

in the trypsin act on the two proteins, since the presence of casein, or of gelatin, inhibits the heat-inactivation of the gelatin-hydrolysing power, or of the casein-hydrolysing power, respectively, of the trypsin used (Fairchild's). W. O. K.

Test for Diffusible Ions. I. Ionic Nature of Trypsin. J. H. NORTHROP (*J. Gen. Physiol.*, 1924, **6**, 337—347).—The ratio of the concentrations of trypsin inside and outside the particles of gelatin suspended in water, is equal to the ratio of the hydrogen-ion concentrations on the two sides between the limits of p_H 2 to 10·2. Above p_H 10·2 the trypsin is distributed in the same ratio as the chlorine ion. Trypsin would therefore appear to be a diffusible amphoteric electrolyte, with isoelectric point at p_H 10·2, giving positive univalent ions below this value and negative univalent ions above it, and to be distributed on the two sides of the surface of the gelatin particles in accordance with the Donnan equilibrium. It would seem to be a strong base below p_H 10·2, as no evidence was obtained of undissociated trypsin. With increasing salt content, the same relations in the concentrations hold. The ratios of the concentrations of trypsin, and of hydrogen- and chlorine-ions all change in accordance with the Donnan equilibrium. W. O. K.

[**Pancreatic Enzymes. V.** R. WILLSTÄTTER and collaborators.] **Enterokinase and the Tryptic Action of the Pancreas.** E. WALDSCHMITZ-LEITZ (*Z. physiol. Chem.*, 1924, **132**, 181—237).—A detailed investigation of the influence of enterokinase on the tryptic hydrolysis of gelatin in which the tryptic activity was determined by a method based on that of Willstätter and Waldschmitz-Leitz (cf. A., 1922, ii, 169). The activation of trypsinogen by the kinase is, in its initial stages, proportional to the time and reaches a constant value, less than the maximum possible degree of activation, in from 30 to 60 minutes according to the amount of kinase present. The speed of activation is greatest in neutral solutions. For any given preparation there is a direct proportionality between the amount of kinase necessary for the final degree of activation attained, and the amount of the enzyme activated. Glycerol and ethylene glycol and substances of autolytic origin have an inhibiting effect on the activation. The preparation of purified enterokinase free from proteolytic enzymes is described. Such preparations are highly specific and have no influence on pancreatic lipase or diastase. The author interprets his results as pointing to a simple activation of trypsinogen by the kinase, and as opposing the view that the process is an enzymic one. Using alumina as adsorbent, it is possible to separate the enzyme and its activator and so convert an active trypsin preparation into an inactive trypsinogen, which may then be subsequently reactivated. The trypsinogen of fresh or dried pancreas becomes "spontaneously" activated on keeping, especially in acid solution. This is regarded not as an autolytic change of the inactive enzyme, but as analogous to the activation by enterokinase, since, like the latter, the substance responsible for the

phenomenon may be adsorbed by alumina and so separated from an active trypsin which is thus reconverted to trypsinogen. The possible identity of this "spontaneous" activator with enterokinase is discussed in relation to the secretion of active pancreatic juice under the influence of pilocarpine and peptone. It is concluded that the activation of trypsinogen by enterokinase is a specific reaction conditioned in part by adsorption, but chiefly by the mutual influence of enzyme and activator on the affinities of specific groups, which is likened to the effect of hydrogen-ion concentration. J. P.

Arginase in Bacteria. S. HINO (*Z. physiol. Chem.*, 1924, **133**, 100—115).—Living *Bacillus pyocyaneus* and *B. fluorescens*, as well as their acetone preparations, act on *d*-arginine. Filtrates from their cultures were inactive. The arginase is more active in the living organisms. The presence of urease in the above organisms has also been established. *Staphylococci*, *B. prodigiosus*, *B. coli*, *B. paratyphosus*, *B. typhosus*, *B. dysenteriæ* (Shiga), and *Streptococci* do not contain arginase. S. S. Z.

Preparation of Dried Urease and Determination of Urea in Normal and Pathological Urines. G. REVOLTELLA (*Biochem. Z.*, 1924, **144**, 229—257).—Improvements are given in the method already described by the author (*ibid.*, 1922, **134**, 336) for preparing dried urease from soya beans. A correction factor of 5·3% must be added to the urea determined by means of urease prepared by the author's old method in view of the incomplete nature of the conversion of urea to ammonium carbonate. Two improved methods for determining urea are described. In the direct method, 5 c.c. of urine and 2 drops of 0·3% methyl-orange are placed in each of two 50-c.c. graduated flasks, and 0·05*N*-sulphuric acid is added until the colour is light orange; 0·25—1·0 g. of urease (according to the activity of the preparation) is added, the solutions are diluted to 50 c.c. with distilled water, and the flasks are stoppered and placed in a water-bath for 1 hour at 45—50°. Ten c.c. of solution from one flask are titrated against 0·05*N*-sulphuric acid to a light orange and the number of c.c. of acid required multiplied by 0·15525 gives the corrected urea content in grams per 100 c.c. The second flask serves as a control on the completion of the fermentation. An improved direct aspiration method for determining the preformed ammonia and urea in urine or in any body fluid is also given, for details of which the original must be consulted. The influence of various normal and pathological constituents of urine, such as uric acid, proteins, amino-acids, dextrose, sodium chloride, and ammonium carbonate, and of varying conditions of temperature, hydrogen-ion concentration, and light, on the urease method of determining urea has been studied. It is concluded that urease methods provide, when properly controlled, the most convenient and most accurate means of determining urea. J. P.

Auxoureases. F. DI RENZO (*Biochem. Z.*, 1924, **144**, 298—302).—Preliminary heating of a solution of urease for periods

varying from 10 to 30 minutes increases the activity of the enzyme, the maximum effect being attained with temperatures of 60—70° using 0·3% solutions of urease. The phenomenon is regarded as being similar to the activating effect of "auxo" bodies such as potassium cyanide and glycine on urease. J. P.

Sulphatase. IV. Enzymic Fission of β-Naphthyl Hydrogen Sulphate. J. NOGUCHI (*Biochem. Z.*, 1924, **144**, 138—140).—β-Naphthyl potassium sulphate was prepared by treating β-naphthol in the presence of pyridine with chlorosulphonic acid dissolved in chloroform, followed by removal of the solvents and neutralisation with potassium hydroxide. The potassium salt, obtained as fine white plates, gave no precipitate in aqueous solution with barium chloride. On incubation with sulphatase (A., 1923, i, 1148; 1924, i, 107), it is hydrolysed to β-naphthol and potassium sulphate. J. P.

Acid Production by *Bac. Granulobacter*. H. B. SPEAKMAN. —(See i, 371.)

Isoelectric Points for the Mycelium of Fungi. W. J. ROBBINS (*J. Gen. Physiol.*, 1924, **6**, 259—271; cf. *Amer. J. Bot.*, 1923, **10**, 412).—Mycelia of *Rhizopus nigricans* and of *Fusarium lycopersici* behaved towards acid and basic dyes similarly to amphoteric colloids with isoelectric points p_H 5·0 and 5·5 respectively. The amount of growth of *Rhizopus nigricans* on potato-dextrose agar and also the dry matter produced when grown on potato-dextrose broth, when plotted against the p_H of the medium, show a double maximum with an intervening minimum at initial p_H 5·2. W. O. K.

Assimilation of Aldehydes by Plants. II. Polymerisation of Formaldehyde by *Phaseolus multiflorus* and *Pelargonium* with the Formation of Higher Aldehydes. T. SABALITSCHKA and H. RIESENBERG (*Biochem. Z.*, 1924, **144**, 545—550).—The above plants assimilate formaldehyde in the dark with the formation of sugar and starch. S. S. Z.

Assimilation of Aldehydes by Plants. III. Does the Presence of Formaldehyde interfere with the Determination of Sugar and Starch in the Experimental Plants of T. Sabalitschka? T. SABALITSCHKA and H. RIESENBERG (*Biochem. Z.*, 1924, **144**, 551—555).—It does not. S. S. Z.

Respiratory Quotient of Roots and its Variation with the Development of the Plant. R. CERIGHELLI (*Compt. rend.*, 1924, **178**, 645—647).—The respiratory quotient for the detached roots of various plants has been determined at different periods of growth. It was always found to be less than unity at the beginning of growth, and with annuals poor in reserve materials (wheat, maize, etc.), it remains so throughout the whole of the growth period. These two facts are the reverse of those observed in the case of the leaves.

As previously found, the respiratory quotient often falls at the time of flowering or of fruit-bearing, or at some time after this. The root in this case behaves analogously to the leaves.

Annuals possessing plentiful reserve materials (radish, lupin, etc.) and most perennials (iris, rhubarb, etc.) give a respiratory quotient greater than unity, except at the beginning of the growth period. E. E. T.

Effect of Phosphates on [Plant] Respiration. C. J. Lyon (*J. Gen. Physiol.*, 1924, **6**, 299—306).—The effect of increasing the phosphate content of the medium upon which *Elodea canadensis* is growing is to increase within about 30 minutes the rate of respiration as measured by the production of carbon dioxide. This effect increases with the concentration of phosphate-ion up to a concentration of 0·1*M*, beyond which it remains constant. When plotted against time it is found that for any given phosphate concentration the rate of respiration rises to a maximum, falls, rises to a second higher maximum, and again falls. The death of the plant occurs during the fall from the first maximum, the subsequent respiration being a *post-mortem* phenomenon. To investigate the anaërobic respiration wheat seedlings were used, and a similar increase in the production of carbon dioxide in the presence of phosphate was observed. W. O. K.

Development of Pentosans in Barley during Germination. M. H. van Laer and A. Masschelein (*Bull. Soc. chim. Belg.*, 1923, **32**, 402—404).—During the germination process a distinct increase in the quantity of pentosans occurs in barley, especially in the embryo and the radicles. The endosperm also shows an appreciable increase. On steeping in water the total pentosan loss is about 4%; this takes place almost entirely from the chaff. Malting also results in the formation of pentosans, but in this case the distribution is not similar, the increase being considerable in the endosperm, whilst it is very small in the radicles. H. J. E.

Absorption of Carbon by the Roots of Plants. J. F. Breazeale (*J. Agric. Res.*, 1923, **26**, 303—311).—Wheat seedlings were grown in a number of different culture solutions, and the plant ashes examined. Carbonates were found in the ash of plants grown in solutions containing sodium or ammonium nitrate, or the carbonates of calcium, sodium, or potassium. The carbonate ion was absorbed by the roots of the plants, but free carbon dioxide could not be taken up in the absence of soluble bases; the rate of absorption of bases depended largely on the absorption of an acid radical. It is suggested that such salts as sodium nitrate influence carbonate absorption as a result of the more rapid removal of the nitrate ion and the subsequent formation of sodium carbonate from atmospheric carbon dioxide. Evidence is advanced that the so-called "lime-loving" plants are in reality those requiring considerable amounts of carbonate. The plant root may maintain equilibrium in its tissues or in the nutrient solution by the intake of carbonate ions or by the excretion of free carbon dioxide. A. G. P.

The Form of Nitrogen most Favourable for Higher Plants. G. TRUFFAUT and N. BEZSSONOFF (*Compt. rend.*, 1924, **178**, 723—725).—An investigation of the effect of various nitrogenous fertilisers on the growth of several common crops in pots and in the field. It is concluded that mixtures containing nitrogen in the form of carbamide are more effective than nitrates, ammonium salts, or even carbamide alone. In acid soils, carbamide–sodium nitrate mixtures, in alkaline soils, carbamide–ammonium sulphate mixtures, appeared to give the best result. In some cases mixtures of this type have enabled the authors to reduce the percentage of nitrogen in the fertiliser from 3% to 2% and yet to obtain an increased yield. E. E. T.

Influence of a Deficiency of Potash on the Development of Barley Manured with different Amounts of Sodium Nitrate. H. WEISSMANN (*Z. Pflanz. Düng.*, 1924, **A**, **3**, 21—24).—Barley was grown in sand cultures, with a potash-free nutrient solution, to which increasing amounts of sodium nitrate were added. The dry-weight of the crop decreased with increasing amounts of sodium nitrate, only those plants having the smallest amount of sodium nitrate in the nutrient reaching the grain stage. The other plants died prematurely. The total intake of potassium by the plants decreased with larger doses of sodium nitrate, but the nitrogen- and sodium-intake increased with the proportion of sodium nitrate in the nutrient. The bearing of these results on the influence of potash-starvation on growth (cf. *ibid.*, 1923, **A**, **2**, 1) is discussed. A. G. P.

Coexistence of Starch and Inulin in certain *Compositæ*. L. DANIEL (*Compt rend.*, 1924, **178**, 726—727).—Starch and inulin have been found to occur together in *Helianthus tuberosus* and *H. multiflorus* grafted on to the sunflower (annual). On one occasion they were both found in an artichoke graft. They were also found in ungrafted plants, *e.g.*, *Jurinea alata* and various species of *Centaurea*. E. E. T.

State of Tannins in the Vegetable Cell. MICHEL-DURAND (*Compt. rend.*, 1924, **178**, 586—589).—Young oak or chestnut plants, on being extracted with acetone, yield, in general, less tannin than when extracted with boiling water. It is concluded that the tannin is present, in the cell, in more or less intimate combination with mucilaginous substances. E. E. T.

Protopectin and some other Constituents of Lemon Peel. R. SUCHARIPA (*J. Amer. Chem. Soc.*, 1924, **46**, 145—156).—The author distinguishes between "free pectin," the soluble jelly-making portion of fruits etc.; "protopectin," the water-insoluble pectin occurring in the cell wall closest to the cellulose layer; and "pectic acid," the ultimate product of hydrolysis of pectic substances.

Protopectin was prepared from the white pericarp of *Citrus limonum*. It gave pectin and cellulose on hydrolysis besides a small amount of impurities, including lignocelluloses that could not be removed previously. Pectins with different methoxly

contents have been prepared from the same source. It has been shown that the cell-wall of the parenchymatous tissue of *Citrus* contains "free" cellulose, which dissolves readily in Schweitzer's reagent, and also cellulose combined with pectin, which becomes soluble only after hydrolysis. An hypothesis is advanced as to the linking of the cellulose and pectin, based on the replacement of the cellulose in protopectin by methoxyl groups. The question of the transition of protopectin to pectin in the cell is discussed. F. A. M.

Constitution of Derris Root. I. S. TAKEI (*Rikwagaku Kenkyujo Ihô*, 1923, **2**, 485—496; cf. Kariyone and Atsumi, A., 1923, i, 477).—When extracted with hot ether, roots of *Derris elliptica*, Benth., grown in Singapore, gave colourless, hexagonal plates, m. p. 163°, which correspond with tubatoxin; the formula was found to be $C_{19}H_{18}O_5$, whilst former investigators gave $C_{18}H_{18}O_5$. Its methoxyl content corresponded with 1·5 methoxy groups in 1 mol.; it gave a phenylhydrazone, yellow needles, m. p. 243—245°. For the rabbit, the minimum lethal dose was 0·00125 g. per 100 g. of body-weight. When treated with concentrated sulphuric acid, it was changed into an *isomeride*, colourless needles, m. p. 177—178°, having no poisonous properties. The saponification of tubatoxin with 3% hot alcoholic potash gave a *phenolcarboxylic acid*, $C_{10}H_{10}O_3$, m. p. 128—129°, which absorbed bromine and gave a violet colour with ferric chloride. When the saponification was conducted in a current of hydrogen, an *isomeride*, colourless needles, m. p. 209—210°, was obtained which had no poisonous action. By fusion with potassium hydroxide, tubatoxin itself or the acids mentioned above gave another *phenolcarboxylic acid*, $C_9H_9O_3$, colourless needles, m. p. 182°. This acid sublimed at about 160°, and is probably a methylated benzoic acid. K. K.

Chemical Analysis of *Jatropha stimulosa*. P. MENAUL (*J. Agric. Res.*, 1923, **26**, 259—260).—The seeds of *Jatropha stimulosa* resemble castor beans, and contain 61% of kernel. The expressed oil had the following characteristics: $d^{15·6}$, 0·9257; $n^{15·6}$, 1·4765; solidifies below −15°; iodine number, 124·65—129·47; saponification number, 186; volatile fatty acids, none; free fatty acids, trace; fatty acids, 95·6%; glycerol about 4·2%. The seeds also contain much protein, the analysis and nitrogen distribution of which has been studied. There is a high histidine content. A. G. P.

Mono- and Di-methylolcarbamide. Their Effect on Plant Growth, and their Decomposition in the Soil. E. BLANCK and F. GIESECKE (*Z. Pflanz. Düng.*, 1923, **2**, 393—420).—When formaldehyde is added as a preservative to liquid manure (urine) containing carbamide, monomethylol carbamide, $CO(NH_2)NH{\cdot}CH_2{\cdot}OH$, and dimethylolcarbamide, $CO(NH{\cdot}CH_2{\cdot}OH)_2$, may be formed. Experiments are described on the effect of these compounds, and also of liquid manure–formaldehyde mixtures, on the growth of plants in sand and soil cultures. Both compounds at first depress the germination of oats and turnips. This effect is, however, followed

by stimulation. Monomethylolcarbamide is equally effective with ammonium sulphate as a source of nitrogen for oats and mustard. Dimethylolcarbamide is generally less satisfactory, and may in some cases be actually harmful. The experiments with liquid manure–formaldehyde mixtures show similar results, large amounts of formaldehyde being injurious. The nitrogen of these compounds is readily ammonified by soil organisms. It is concluded that whilst formaldehyde may be used as a preservative with liquid manure, excess should be avoided. G. W. R.

Nature of the Activity of the Colloidal Clay of Acid Soils. R. BRADFIELD (*J. Amer. Chem. Soc.*, 1923, **45**, 2669—2678).—In this investigation, standard solutions of sodium hydroxide and calcium hydroxide were titrated with the colloidal material from four acid soils and the end-points determined by both conductivity and hydrogen-ion concentration measurements (cf. *ibid.*, 1923, **45**, 1245). The end-points found by both methods were fairly definite, and the titration curves were of the type commonly obtained in the titration of a strong base by a weak acid. The same amounts of the colloidal acids were required to neutralise equivalent quantities of the two bases, and definite breaks were obtained in the conductivity curves, indicating the neutralisation of definite acids. The reaction between acid colloidal clays and strong bases appears to be an ordinary neutralisation. The results obtained tend to show that the colloidal material of an acid soil is itself an acid which ionises to produce a definite Sörensen value and which shows a definite titrable acidity on titration with strong bases. F. G. P.

Soil Reaction in Relation to Calcium Adsorption. C. O. SWANSON (*J. Agric. Res.*, 1923, **26**, 83—121).—The adsorption of calcium and the alterations in soil reaction, following the addition of lime to a number of soils, are described. Potassium chloride was found to reduce the adsorption of calcium in soils unless relatively large amounts of calcium carbonate were present. Soil suspensions showed lower p_H values than filtered soil extracts. The adsorption of calcium by soils was more intimately connected with the clay content than with the original hydrogen-ion concentration of the soil. Fuller's earth had a greater hydrogen-ion concentration and a greater adsorptive power than any soil examined. Leaching with water did not affect the adsorptive power or p_H value of soils. The presence of calcium carbonate did not influence the calcium adsorption from calcium hydroxide. Dilute hydrochloric acid increased the hydrogen-ion concentration of soils to an extent proportional to the amount of acid. Small additions of oxalic acid to soil decreased the hydrogen-ion concentration and larger amounts increased this figure, but to a less extent than did equivalent quantities of hydrochloric acid. Acidity of mineral soils is attributed to the leaching out of bases leaving acid alumino-silicates, which readsorb soluble bases (particularly calcium), leaving an insufficient supply for the normal growth of plants. A new apparatus for determining hydrogen-ion concentrations of soils is described. A. G. P.

Partial Sterilisation of Soil by Antiseptics. (Mrs.) A. Matthews (*J. Agric. Sci.*, 1924, **14**, 1—57).—An examination is recorded of the microflora in soils treated with a number of organic antiseptics. The normal effect of antiseptics—an initial decrease in bacterial numbers followed by a sudden rise, which was maintained for varying periods and finally tended to return towards normal—was observed. The antiseptics disappeared from the soil fairly quickly. Aëration increased the rapidity of these changes. The extent of the increase in bacterial numbers varied according to the molecular weight and heat of combustion of the antiseptics used, and some correlation with the latter factor is indicated. Bacterial changes seemed in no way connected with protozoa and occurred in a normal manner even in protozoa-free soils. Increases in bacterial population are ascribed to the feeding effect of the antiseptics or the bacteria, and the improved fertility following partial sterilisation to the breaking down of soil organic matter by the increased number of organisms. The action of lime and of steaming in increasing the bacteria is assumed to result from improved conditions, due to the breaking down of plant residues, etc. Aliphatic compounds produce quicker but smaller changes than aromatic ones. Among aromatic compounds, the introduction of the $-CH_3$ group into the benzene ring lessened the toxicity of the compound to soil organisms, whereas $-Cl$ and $-NO_2$ produced increased toxicity and stability in the soil. The toxic effects of a number of antiseptics on protozoa, eelworm, and fungi are recorded.

A. G. P.

The Manurial Properties of Lead Nitrate. R. A. Berry (*J. Agric. Sci.*, 1924, **14**, 58—65).—A number of culture and field experiments are described in which lead nitrate was used as the source of nitrogen to plants, in comparison with sodium nitrate. Similar yields were obtained by both treatments. The lead salt tended to produce plants with wider leaf blade and of slightly darker colour. When used in commercial quantities, no lead was found in the plants produced, nor could any be leached from the soil. Except when high concentrations were used, lead was adsorbed and rendered non-toxic by the soil. It would appear probable that lead salts increased the rate of nitrification in soils.

A. G. P.

Action of Sodium Nitrite in the Soil. R. H. Robinson (*J. Agric. Res.*, 1923, **26**, 1—7).—Experiments are described demonstrating the unsuitability of sodium nitrite as a fertiliser, particularly on acid soils. In all soils examined, there was a steady loss of nitrogen from the nitrite, only a small proportion of which became oxidised to nitrate. This loss was much accelerated in acid soils. The addition of lime or calcium carbonate to such soils retarded the decomposition of nitrites, but no increased nitrate content could be observed.

A. G. P.